PRETREATMENT OF AQUEOUS PHASE OF MINE PLANT TAILINGS FOR SUBMARINE DISPOSAL

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A

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Abstract

Submarine disposal of mine tailings is a relatively recent technology that holds the promise of solving the recurring problems that the mining industry has had with tailings disposal. The system has been successfully implemented in many mines around the world. Before implementation, however, a decision needs to be made whether the biogeochemical characteristics of the area selected for submarine disposal and characteristics of the tailings are conducive to implement submarine disposal of tailings. While an expert system can decide the feasibility of submarine tailings disposal (STD) based on its database of information and decision loops for the critical factors, tailings cannot be disposed of under water without pretreatment, which is the focus of this thesis. Bioremediation, freeze concentration and reverse osmosis were examined as possible alternatives for treatment. Laboratory tests were performed for all the methods, and in the case of bioremediation, pilot scale tests were also performed. It was concluded that all the three methods remove dissolved metals from mine water to varying degrees. Reverse osmosis was found to be the most efficient method, while freeze concentration was the least efficient method.

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CHAPTER I
INTRODUCTION

"Pretreatment of Aqueous Phase of Mine Plant Tailings for Submarine Disposal" is a project funded by the United States Department of the Interior – Minerals Management Service. The project is being carried out at the University of Alaska – Fairbanks.

1.1 Motivation

In a mining operation, disposal of plant tailings, both aqueous and solid, is an important design consideration. The conventional way of disposing tailings is to sequester them in a tailings pond or a tailing stack. This has the following disadvantages:

- This method is space intensive and requisition of large tracts of land is necessary for its implementation.
- Tailings disposed on the surface can be carried to the local water streams by wind or rainwater. This can elevate the danger of contamination of these water streams. Mobile heavy metal ions, which constitute a large part of the tailings, can also enter the human food chain through the local fish population.
- Alaska is a seismically active zone. Seismic activity might destabilize the tailings stacks and rupture tailings dams, thus resulting in widespread contamination.

In the light of the aforementioned problems submarine tailings disposal (STD) may become an attractive option for mines in coastal areas. The advantages of submarine disposal of tailings are as listed below:

- Submarine disposal is not land intensive.
- The solid phase of mine tailings cannot be oxidized in a submarine environment, as water near the sea floor has anoxic conditions. Some metals can be mobilized through oxidation.
- Once placed in the naturally occurring valleys or depressions on the ocean floor, tailings should be stable, even in case of seismic activity.

- Submarine disposal of tailings may be cost effective.

The state of Alaska has the longest coastline in the Unites States. Alaska is also a highly mineralized zone, with mining being one of the most important industries. Many mines, e.g., the Teck-Cominco Red Dog mine and the Kennecott Greens Creek mine are located sufficiently close to the coast to take advantage of submarine disposal for their tailings. There are several examples of STD being employed as a solution to tailings disposal problems. Island Copper Mine on Vancouver Island, British Columbia, Canada employed the first large scale system for STD (Marine Tailings Disposal; Ellis, D.V. Ed.; 1982). Other mines that practiced STD include the Atlas Copper Mine, Cebu Island, the Philippines; Batu Hijau, Sumbawa Island, Indonesia; and Minahasa Raya, North Sulawesi, Indonesia (Ganguli *et al*, 2002). This project focused on providing feasibility and selection criteria for STD as well as pretreatment options for mine mill tailings with emphasis on minimizing environmental impacts.

1.2 Background

There are several environmental concerns about the application of STD. The United States Environmental Protection Agency (USEPA) precludes STD as a general rule. The potential impacts of STD are:

- Physical – Change in turbidity and color characteristics of water in the discharge zone.
- Biological – The effect of the discharge on the flora and fauna of the sea bed. The discharge might alter the physico-chemical environment for the benthic species.
- Chemical – The discharge might affect the chemical composition of sea water. Alterations in the level of salinity, dissolved ions and concentration of toxins, both organic and inorganic, may be expected.
- Long Term Environmental Concerns – As a cumulative effect of the factors mentioned above, change in the biogeochemical characteristics of the sea bed may be possible.

Ellis states that the environmental risks from STD can be grouped into four categories. They are: water column turbidity, seabed smothering, toxicity and trace metal contamination (Marine Tailings Disposal; Ellis, D.V. Ed.; 1982).

Thus, apart from biological, oceanographic and seismological studies of the sea bed for potential STD, it is important that the mill tailings be also characterized with respect to their chemical composition and pretreatment options be examined.

1.3 Expert System for STD (STADES)

In order to synchronize the engineering design concerns of STD with the environmental requirements, Ganguli *et al.* (2002) designed an expert system, which is a knowledge-based computer program that uses knowledge in the form of a database and decision making loops to solve problems that require human judgment. The expert system is schematically illustrated in Fig 1.1.

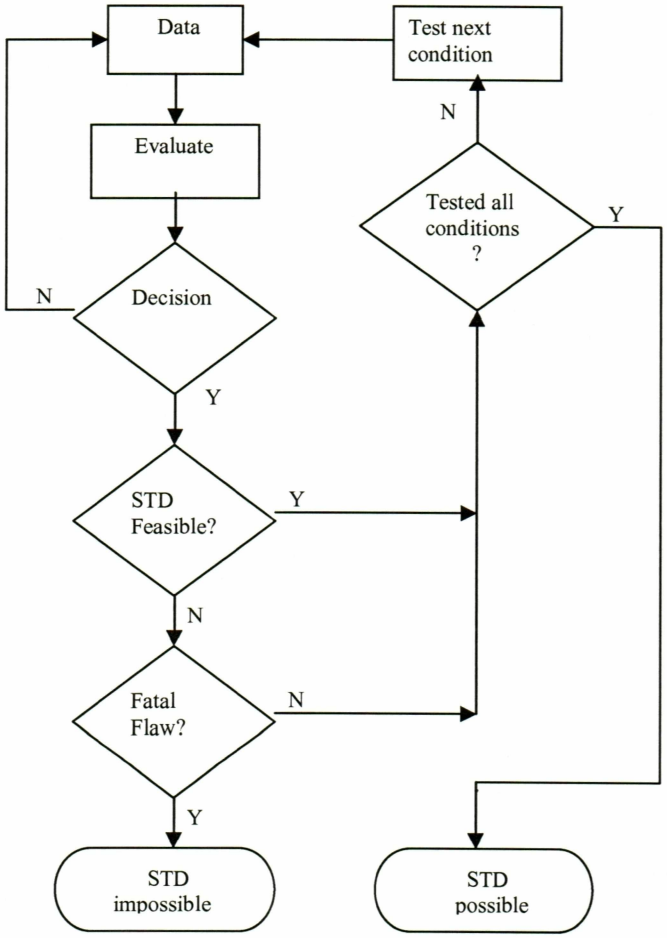

Fig 1.1 : Expert System Model (Ganguli *et al.*, 2002)

This system was first developed with the help of the expert system software LEVEL 5. This software was chosen as it combines expert system capabilities with object oriented programming systems, relational data base models, hyper-text capabilities, and graphical development and debugging tools. It provided an independent window based interactive system. It would perform critical physical checks (depth of disposal, reservoir capacity, plunge angle etc.) and environmental checks (release potential and bioavailability of ions), and would then decide if STD was feasible in the given case.

This expert system was a useful tool for the preliminary exploration of STD. But LEVEL 5 is proprietary software and thus requires a license to operate. Also, pretreatment of the tailings was not considered in the model. The decision was then made to switch the model to a Visual Basic base for ease of application and a module for pretreatment of tailings was planned for.

Three methods for pretreatment of tailings for STD were explored. These were:

- Bioremediation
- Freeze Concentration
- Reverse Osmosis

Experimentation on these three methods was the focus of this thesis.

Five metals were selected for remediation. They are:

- Lead
- Zinc
- Cadmium
- Iron
- Manganese

These metals were chosen as they are some of the most widely available metals in solution in mine tailings.

CHAPTER II

LITERATURE REVIEW

2.1 Introduction

In this chapter, a brief literature review is conducted on the selected methods of remediation, i.e., bioremediation, freeze concentration and reverse osmosis. Some of the papers are important sources of information and others for experimental procedures. Many have served as guidelines for the experiments conducted for this thesis. The most prominent among such papers are reviewed here.

In recent years environmental concerns have come to the forefront for all industries. Mining, an industry where the exploitation of natural resources inevitably causes the dislocation of the environment from its natural state, has been under much scrutiny. Mining causes defoliation of previously virgin forest land, causes subsidence (in the case of underground mining) and huge cavities in the land in the case of surface mining. Mining also has the potential to cause significant air and water pollution. In this thesis, remediation of polluted water is the primary focus. The contribution of mining to pollution of local water bodies is primarily by intermixing of local water resources with the mine runoff water, which transports contaminants, both metallic and non-metallic, from the mining area into the aquatic environment. Mine runoff water is generated mainly by the following ways:

- Mining, more often than not, punctures, or draws from, the local groundwater table. Such a large influx of water causes a hindrance in operations and can also be lethal for personnel; therefore suitable precautions are taken to avoid such accidents. Underground mines may be designed with a low slope to its ramps so that water may either flow freely out of the mine into the main tailings pond, or into a sump inside the mine from where it is pumped to the tailings pond. Surface mines usually use a system of pumps at the lowest bench in order to achieve the same goal. This water, having been close contact with the mineral body, is can be laden with a high concentration of metallic and non-metallic contaminants.

- Runoff from precipitation can also transport high quantities of dissolved and suspended solids into the water bodies of the area.
- A significant quantity of water is used in mines, particularly in drilling, which adds to the total volume of water discharged from the mine.
- Processing plants associated with mines use and discharge large quantities of wastewater. Processes like floatation generate a lot of contaminated water; while pressure filters filtering slurry will squeeze out contaminated water and discharge it eventually into tailings ponds.
- Finally, contaminated drainage can also occur naturally through the oxidation of exposed pyrite ores in a mineral rich area. The ore may be exposed naturally, or by occurrence of natural disasters like earthquakes, or fluvial or wind erosion. Ore may also be exposed due to mining activity, i.e., residual ore at the end of mine life, or residual ore in the waste pile.

Such toxic wastewater from a mine is generally termed as Acid Mine Drainage (AMD) or Acid Rock Drainage (ARD). During the life of the mine, AMD is channeled to the tailings pond. The supernatant water in the tailings pond is then drawn and treated before discharging into the surrounding environment. Lintern (1994) gave a schematic representation of Natural AMD as described in Fig 2.1.

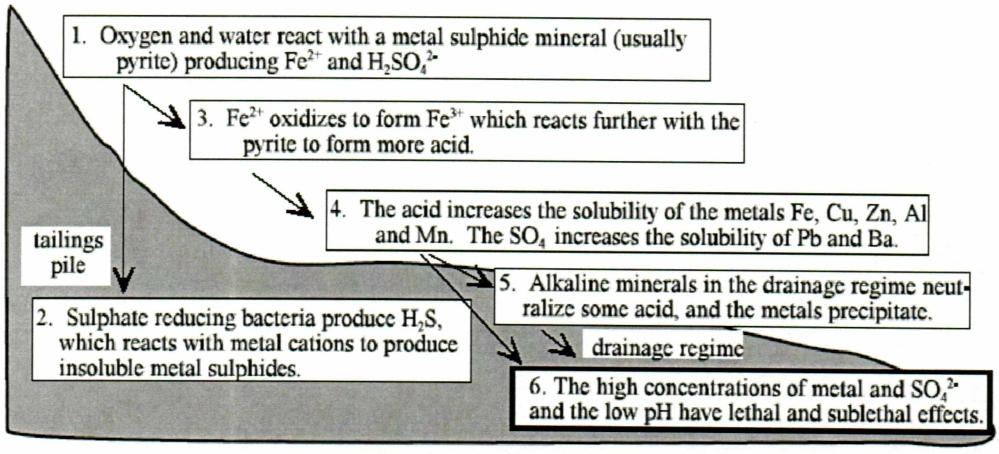

Fig 2.1: Process of natural AMD formation (Lintern, 1994)

Fig. 2.1 is a simplified schematic diagram of the formation of natural acid rock drainage. Many heavy metals occur as pyrites. Pyrite rock, when exposed to air and water, Fe^{2+} and sulfuric acid. The sulfuric acid increases the solubility of metals like iron, cupper, lead, zinc, manganese etc. Thus the effluent water has low pH and high concentrations of dissolved metals. Though alkaline minerals present in the drainage basin might neutralize some acid, the low pH and high metal content still causes significant damage.

The United States Environmental Protection Agency (EPA) maintains strict guidelines regarding the concentrations of the contaminants allowable in such discharge water. Company policies regarding discharge water are formulated to meet the EPA criteria. To take an example in Alaska, the Red Dog Mine in northern Alaska, (location given in Fig. 2.2) discharges all its post treatment water into Red Dog Creek. The Water Quality Standards document number 18 AAC 70 published by the Alaska Department of Environmental Conservation (as amended through June 26, 2003), sets the following parameter for the water quality in the Red Dog Creek. Red Dog Creek, located near Red Dog Mine, should be monitored on the basis of concentration of dissolved inorganic substances as the main criterion. Total Dissolved Solids (TDS) in the water, with calcium greater than 50% by weight of total cations, may not exceed 1500 mg/l and may not exceed 500mg/l during the spawning season for Arctic Grayling which is noted to be late May to mid-June (pages 39 – 40, 18 AAC 70). If Calcium is less than or equal to 50% by weight of the total cations, the total TDS may not exceed 1000 mg/l. The document also states that any concentration of TDS that could cause or could be expected to cause adverse effects on the aquatic life cannot be present in water (pages 39 & 8, 18 AAC 70). This means that Red Dog Mine authorities cannot discharge any concentration of TDS in Red Dog creek water if it unbalances the natural concentrations of inorganic substances in the water.

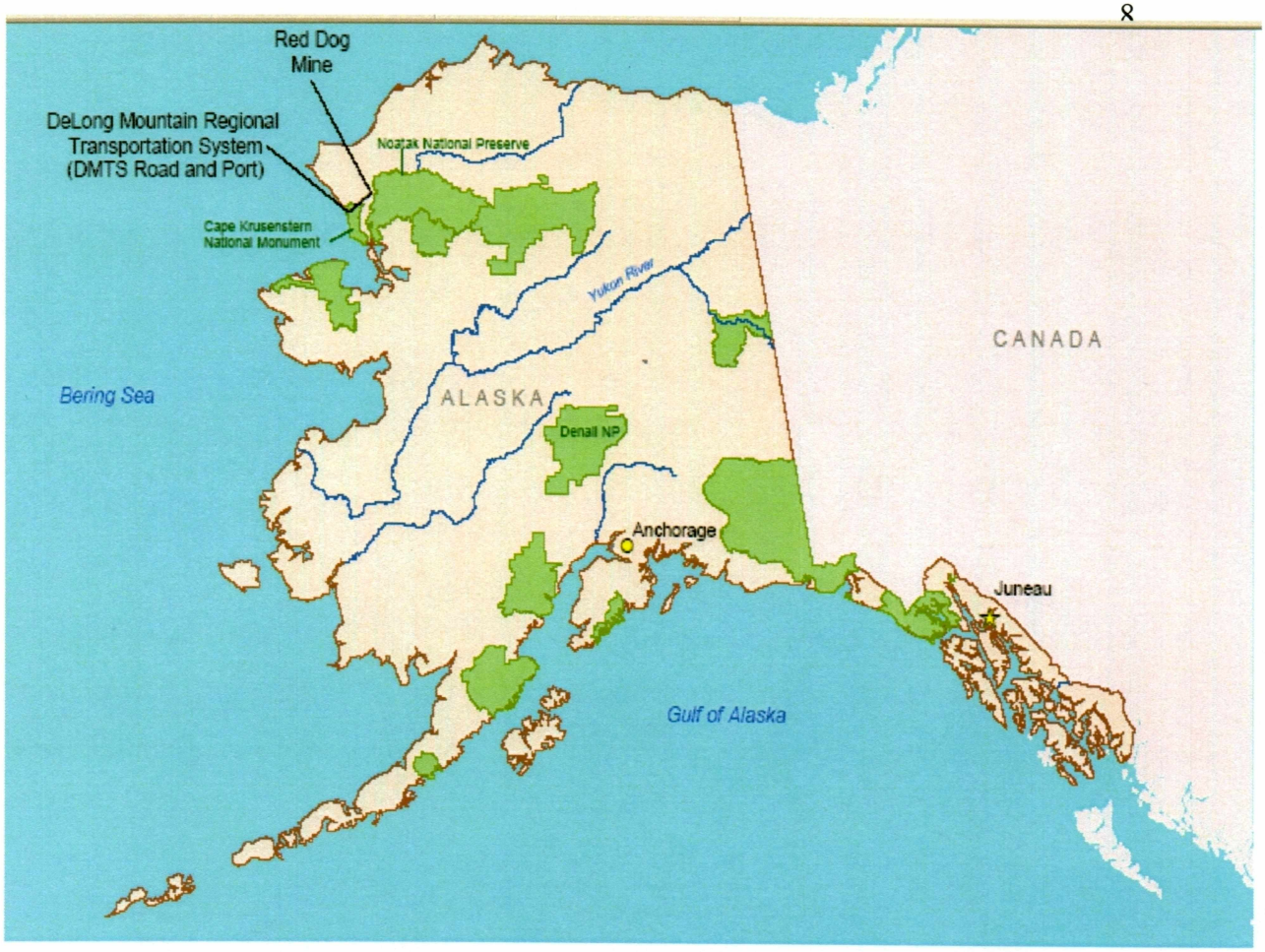

Fig – 2.2: Location of Teck-Cominco Red Dog Mine Alaska

Let us now look at the maximum allowable concentration for the five chosen metals, lead, zinc, cadmium, iron and manganese. EPA document 833-R-04-002B, entitled "Local Limits Development Guidance Appendices", published in July 2004, lists all the Clean Water Act Priority Pollutants and the Federal Water Quality Criteria (Appendix D). The appendix lists lead, zinc and cadmium as priority pollutants, and manganese and iron as non priority pollutants. The concentrations are expressed in terms of Criteria Maximum Concentration (CMC) and Criteria Continuous Concentration (CCC).

CMC is defined as follows: The Criteria Maximum Concentration is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed to briefly without resulting in an unacceptable effect.

CCC is defined as follows: The Criteria Continuous Concentration is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect. Tables 2.1 and 2.2 enumerate the CMC and CCC for the five metals (pages D-2 & D-12, EPA document 833-R-04-002B).

Table 2.1: Allowable concentrations for priority pollutants

Priority Pollutant	Freshwater		Saltwater	
	CMC(μg/l)	CCC (μg/l)	CMC (μg/l)	CCC (μg/l)
Cadmium	4.3	2.2	42	9.3
Lead	65	2.5	210	8.1
Zinc	120	120	90	81

Table 2.2: Allowable concentrations for non-priority pollutants

Non-Priority Pollutant	Freshwater		Saltwater	
	CMC (μg/l)	CCC (μg/l)	CMC (μg/l)	CCC (μg/l)
Iron	N/A	1000	N/A	N/A
Manganese	N/A	N/A	N/A	N/A

Note: N/A → Not Available.

Most recent limits for Cadmium, however, are given by the Clean Water Act (U.S.E.P.A. website: http://www.epa.gov/waterscience/criteria/wqcriteria.html) as in Table 2.3:-

Table 2.3: Allowable concentrations for priority pollutant cadmium

Priority Pollutant	Freshwater		Saltwater	
	CMC (μg/l)	CCC (μg/l)	CMC (μg/l)	CCC (μg/l)
Cadmium	2	0.25	40	8.8

It can be said, therefore, that for these five metals, the numbers in Tables 2.1, 2.2 and 2.3 are the maximum allowable concentration in mine discharge water.

Wildeman *et al.* (2003) proposed a decision tree that uses simple physical and chemical tests to determine if a mine waste poses a toxicity threat to the aquatic environment. For the chemical component of the decision tree, leachate tests developed by the US Geological Survey (USGS), the Colorado Division of Minerals and Geology (CDMG), and modified 1311 Toxic Characteristic Leaching Procedure (TCLP) test of the EPA were extensively used. The primary analytical method was Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Twenty five samples of sediments and water flowing over the sediments were collected from two sites in Colorado. Basic analytical measurements were made in the field, and then the samples were analyzed for 31 elements by the ICP-AES. When the pH of the water was less than 5, the element concentration patterns for all the elements were quite similar and toxicity was clearly indicated for elements like lead, copper, zinc, manganese and aluminum. But for a pH greater than 5, it was found that the only dependable test was the TCLP test. The reason for this was found to be that the TCLP test dissolved carbonates and oxides of certain elements while in the other two tests, the same elements were not very easily dissolved and released into solution. This decision tree, as shown in Fig 2.3, though at verification stage, can be effectively implemented to determine the toxicity of the mine waste pile to the surrounding aquatic environment. The information gathered from this model can serve as a useful additional marker in determining the extent to which contaminants should be removed from discharge water.

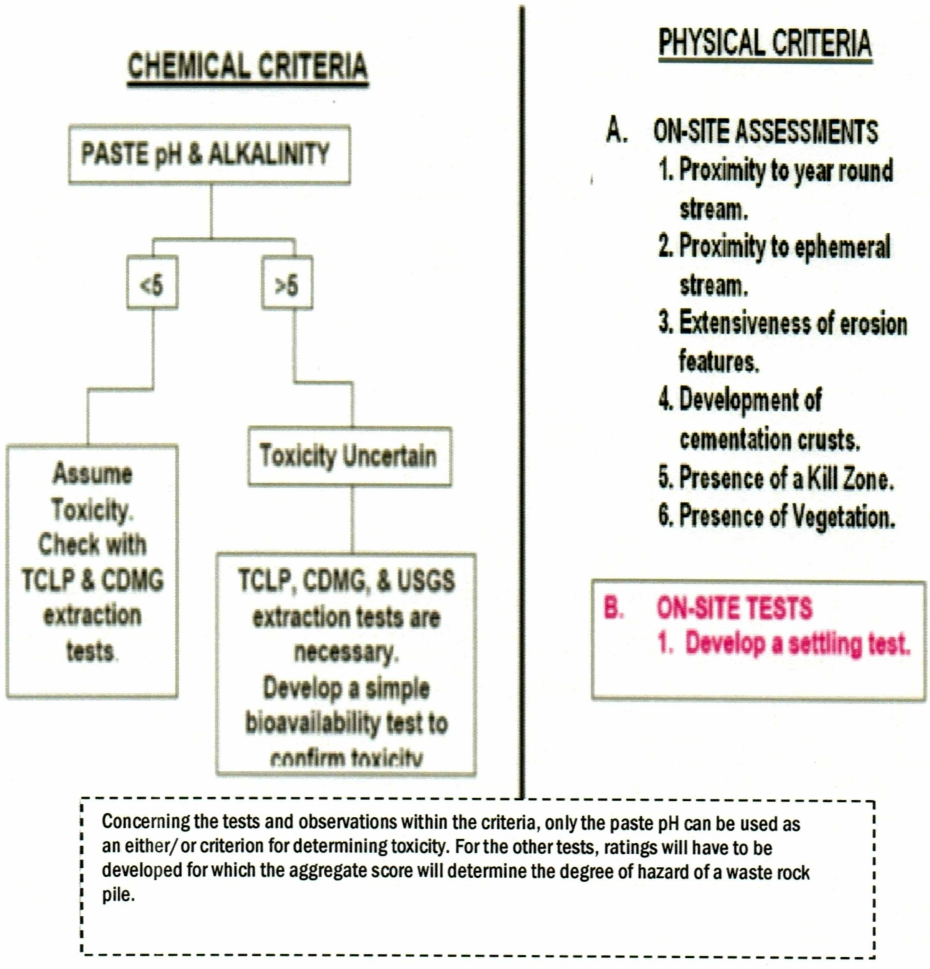

Fig - 2.3: Toxicity Decision Tree (Wildeman *et al.* 2003)

2.2 Literature Review on Bioremediation

In order to remove metals, the first technique attempted was bioremediation. Bioremediation primarily proceeds through anaerobic bacterial action, aerobic bacterial action and sorption (Seyler *et al.* 2003; Unten *et al.*, 1998). Aerobic bacterial environment is quite different from an anaerobic environment and metal is removed by different sets of reaction. The aerobic system, most often implemented as a constructed wetland, removes metals (e.g. Fe(III) and Mn(IV)) by oxidizing them, as metallic oxides are relatively insoluble. Anaerobic processes, including sulphate reduction, are efficient in removing metals like Cu, Zn, Cd, Pb, Ag and Fe(II). Both processes can neutralize acids, increase pH and add alkalinity in the form of carbonates to water thus creating the possibility of removing Al or Cr as hydroxides and Zn and Cu as carbonates.

The anaerobic process is explained by Unten *et al.* (1998). The set of reactions most important to Bioremediation by an anaerobic process using Sulphate Reducing Bacteria (SRB) are given as:

i) Hydrolysis of cellulose

$(C_6H_{10}O_5)_n + n\ H_2O \rightarrow n\ C_6H_{12}O_6$ (eq. 1)

ii) Fermentation

$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$ (eq. 2)

$C_6H_{12}O_6 \rightarrow 2\ C_3H_4O_3 + 2\ H_2$ (eq. 3)

iii) Methanogenesis

$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$ (eq. 4)

iv) Sulphate Reduction

$2\ H^+ + SO_4^{2-} + 2\ \text{“}CH_2O\text{”} \rightarrow H_2S + 2\ H_2CO_3$ (eq. 5)

v) Metal Reduction (Iron)

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (eq. 6)

Metal reaction can be also expressed (Lintern,1994) as

$M^{2+} + H_2S \rightarrow MS\downarrow + 2\ H^+$ (eq. 7)

Eq. 7 is possible because H_2S is a very strong reducing agent.

The process is given schematically by Seyler *et al.* (2003) as shown in Fig 2.4.

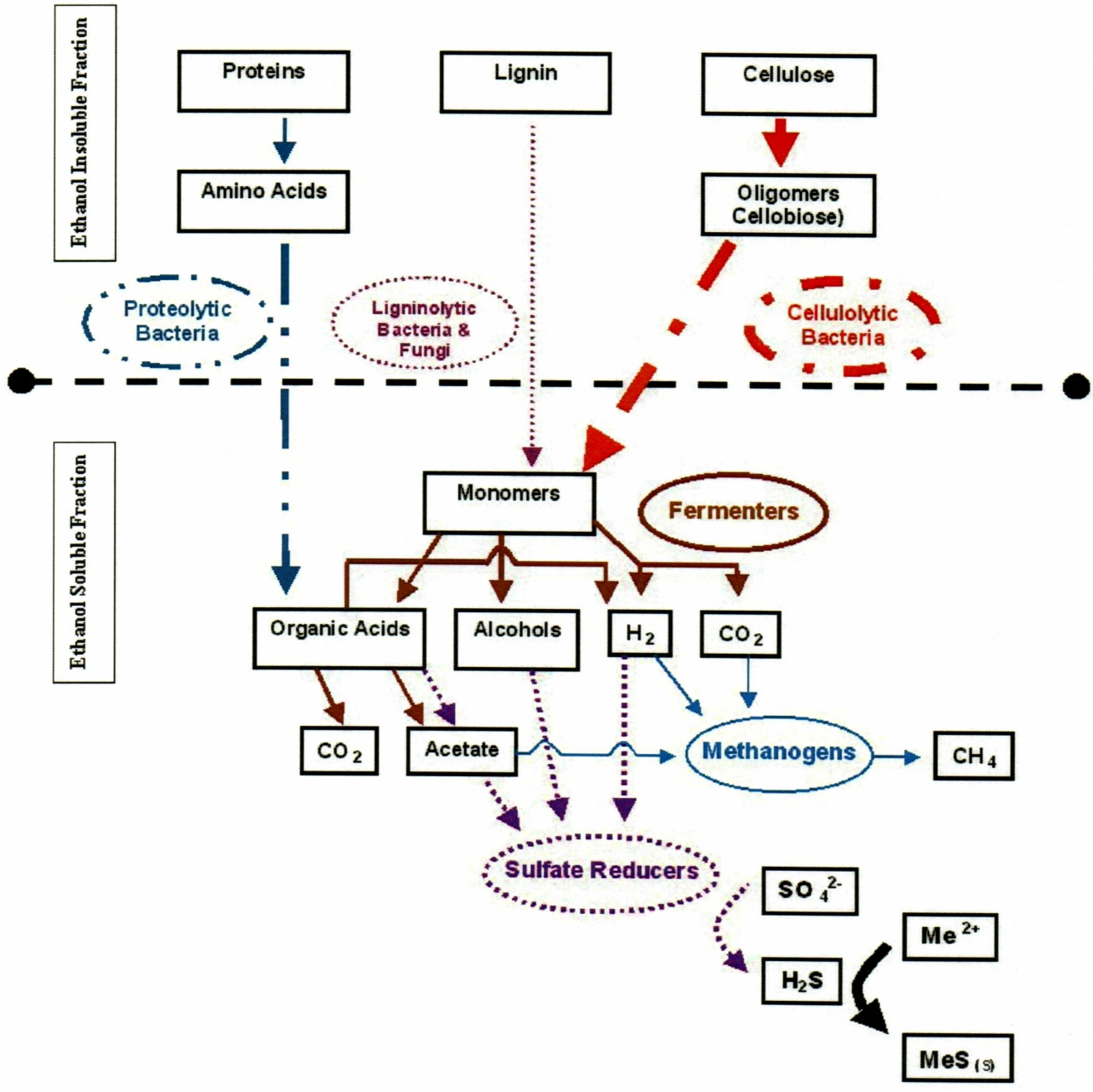

Fig – 2.4: Schematic Representation of Bioremediation (Seyler *et al.*, 2003)

Unten *et al.* (1998) also sets the following guide lines for success in anaerobic reduction of metals.

- Wetland substrates are so formulated that the hydrocarbons required for sustenance of the bacteria are abundant and the soil has a buffering capacity for pH above 7.
- Microbial processes that convert strong acids into weak acids should be promoted.
- Metals are removed by precipitation as sulphides.
- To be viable, it has to be ensured that the reactions increasing the pH are dominant over the reactions producing H^+ ions.

The bacterial strain involved in anaerobic treatment is most likely *Desulphovibrio* though complete knowledge of the microbiology of the system is not at hand yet (Canty; 2000) Johnson and Hallberg (2005) report that on all occasion that the effluent water from compost bioreactors was examined, moderately acidophilic iron reducing bacteria dominated. Sulphate reducing bacteria growing in very low pH were obtained in lesser numbers. Johnson and Hallberg (2003) reviewed the difference between the microorganisms found in different types of acidic environments. They stated that in extremely acidic environments (pH<3), both *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* are known to have been found, and *Thiomonas* and *Acidiphilium* types of bacteria are also common. In hyperacidic mine water (pH $\approx$- 4)*, *At. ferrooxidans* and *L. ferrooxidans* were found to be present. But the dominant genre of bacteria in this case was of the *Leptospirillum* genus.

The principle of anaerobic bioremediation has been proved by many experiments, both at laboratory and field scale. Some of the related papers are discussed below.

Unten *et al.* (1998) conducted the anaerobic experiments in 150ml screw cap culture bottles, which were incubated on a sunny window ledge under ambient conditions of temperature and pressure in the lab for 5 weeks. The inocula for SRB were collected as cattle manure and several kinds of substrates, including mine soil, limestone and algal solution from seepage ponds were used.

***Note:** pH $\approx$- 4 is highly unlikely.

The waters treated were waste pile drainage containing very high concentration of iron, arsenic and selenium, and seepage and underdrainage from a mill tailings facility that has very high concentrations of cyanide, nitrate, ammonia, mercury arsenic and selenium.

Post treatment results indicate that pH was raised from 2 to above 7 and the concentrations of cadmium, chromium, selenium and zinc were reduced to drinking water levels. Iron and arsenic were reduced by about 95% but were not brought to drinking water standards. Manganese was reduced to 50% to 80%.

Christensen *et al.* (1996) used a bench scale setup to investigate bioremediation by SRB. The reaction vessels were transparent polyacrylate cylinders with inner diameter 20 cm and length 100cm with a 7 cm layer of quartz sand and a 25 cm layer of crushed gabbro rock taken from the mine area. The mine water used was heavily polluted water from local mines. Cow manure and artificial cultures were used as inocula, and dairy whey was used as a source of organic carbon. The setup was sealed and incubated for 203 days at 15° C. Fig 2.5 is a diagram of the setup.

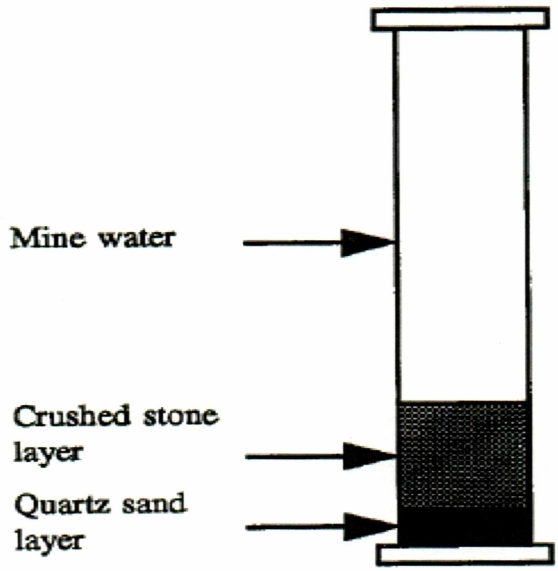

Fig - 2.5: Experimental Setup according to Christensen *et al* (1996).

Samples were taken on days 0, 19, 54, 99 and 203. Mixed results were obtained regarding the final concentrations of metals in the effluent. Copper, zinc, iron and aluminum removal using the artificial inoculum was fast and efficient, but calcium showed a trend to increase in concentration. An increase in dissolved sulphate was also seen across the board. The most likely explanation for this given by the authors is that a reducing condition prevailed after the initial precipitation of iron hydroxides. Acetate was detected in the water, which indicates that fermentation was dominant over complete oxidation of the substrate, a sign that bacterial anaerobic reactions are being favored.

Glombitza (2001) used methanol as an energy source for the bacteria in order to remove sulphates. The mine water was pretreated with Na_2S to remove heavy metals. This was the primary method of heavy metal removal in this case.It was seen that at a residence time of 20 hr, 2000 ppm of heavy metals were nearly completely removed. The bacteria consumed about 1 gm of methanol per gm of sulphate reduced, as opposed to the theoretical value of 0.53 gm of methanol per gm of sulphate. This can be explained by the presence of competing non-SRB in the mixture. Based on this result, a pilot plant for the process was envisaged. The schematic diagram is given in Fig 2.6.

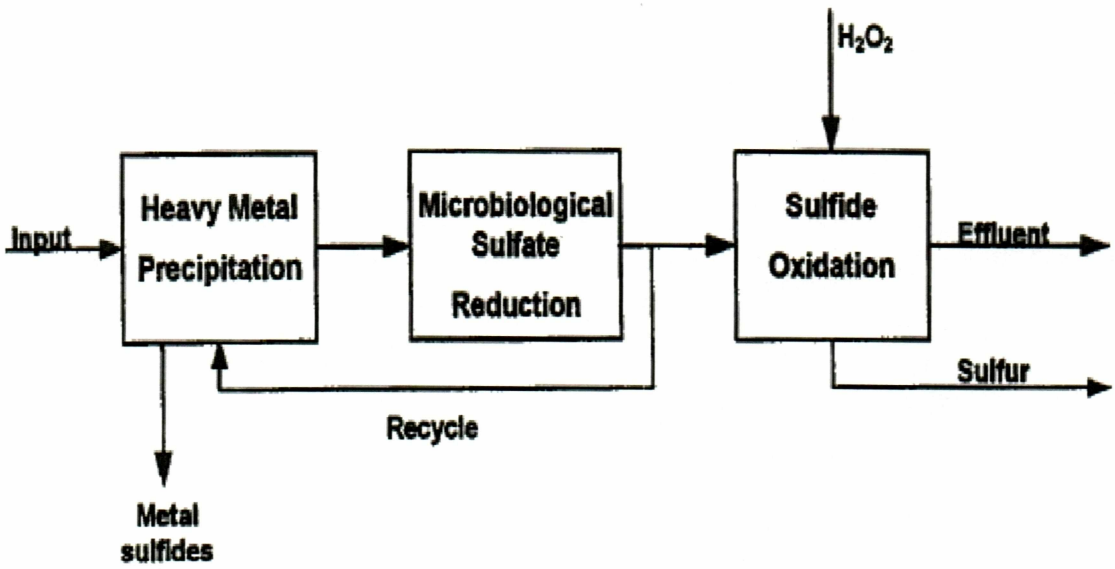

Fig – 2.6: Pilot Plant design according to Glombitza (2001)

The redox potential of the water was set to -150 mV and then pumped into the reactor. The reactor was inoculated with 70 liters of artificial SRB culture. After an initial lag of 2 weeks the concentrations of the sulphates dropped sharply in the reactor. Performance of the system increased due to continuous operation after the development of an SRB biofilm. At the end of the test, a hydraulic residence time of 4.2 hr. was reducing 134 mg/(liter hr) of sulphates, and the consumption of methanol per gm of sulphate reduced went down from 5 gm to 1 gm. Heavy metal removal was almost 100% in this system.

Some research has been done regarding field implementation of bacterial remediation in the industry. Field scale plants have been set up and their performance analyzed. Gusek *et al.* (2000) reported the analysis of a passive bioreactor system situated at the West Fork Lead Mine in Missouri. The water effluent from the mine had a pH of about 8.0 and contained 0.4 – 0.6 ppm lead and 0.36 ppm zinc. The water was pumped at 1200 gpm into a two cell bioreactor of each with a bottom area 1390 sq. m. and a top area of 1930 sq. m. The cells were lined with HDPE fabric. The substrate was composed of cow manure, saw dust, inert limestone and alfalfa. A settling pond settles coarse particles in water before it is pumped to the cells. A rock filter removes particulates from the water after treatment in the bioreactor cells, whereupon the water was channeled to an aeration pond. From the aeration pond the water is discharged into the river. From the settling pond onwards, all the flow is by gravity. The estimated cost for building the system was $ 500,000, with 2 – 3 months of construction time. Operations costs include periodic water monitoring costs; no additional reagent cost is incurred.

Initially the full flow through the cells was blocked by trapping of H_2S gas within the substrate by the retainer fabric put in place to ensure horizontal flow of the water. This problem was solved by releasing the gas by opening control valves, and later by ripping through the fabrics using a excavator. The biggest maintenance problem was

the caking of the top of the bioreactor cells with particles carried by the water, and periodically operations had to be ceased to break up the cake to permit smooth flow.
A significant decrease in the metal concentrations in the water was noted, Lead was reduced from 0.4 ppm to 0.027 – 0.050 ppm, zinc from 0.36 ppm to 0.055 – 0.088 ppm and cadmium from 0.003 ppm to less than 0.002 ppm. pH came out to be in the neutral range (6.63 – 7.77).

It was noted by the authors that the system was quite effective in removing metals, but was not maintenance-free. Future designs, therefore, would have to include measures against clogging. The authors also provide information regarding the performance of the cells at low temperatures and at very high concentrations of metals and low pH.

Canty (2000) reported bacterial treatment of contaminated water at the Lilly/Orphan Boy Mine, located at the Elliston mining district of Powell County, Montana. This abandoned mine consists of a 250 ft shaft which was flooded with AMD to the 74 foot level. Discharge from the shaft was about 11.4 l/min of pH 3 water. The water contains high concentration of As, Zn, Cu, Cd, Fe, Mn and sulphates.
Two platforms with biological substrates were suspended 30 ft below the static water level and secured at the surface with cables. In addition, two intercept wells were drilled at the Lilly tunnel and bio-substrates were placed in this underground space. So effectively, the AMD flowed upward and horizontally through the substrates before emerging into the environment. The experiment started in August 1994, and 4 years of monitoring data are presented here.

The flow rate observed was less than 7.6 l/min, except during spring runoff, when it shot up to 26.5 to 30.3 l/min. pH rose to 7 throughout the 4 years of monitoring, except during spring runoff, when it dropped to 3.5, but restoring itself after spring every time. Aluminum, cadmium and copper were removed very efficiently (85 – 100%). Zinc was removed consistently at 70% and manganese at around 20%. All the metals underwent a drastic reduction of removal efficiency during spring runoff.

Dissolved iron concentrations were increased during normal flow, but appeared to be lower during high flow of the spring runoffs. The results provide an encouraging view of the possibility of metal removal in underground mines by SRB reduction. However, in this case, effect of temperature on the reactions is not provided. It is quite possible that low temperatures will inhibit bacterial growth. Also, the life of the reactor cannot be deduced from the data.

Bioremediation thus proved to be a valid method for reducing metallic contaminants, and was shown to be implementable in a wide variety of field situations.

2.3 Literature Review on Freeze Concentration

Separation of solutes by freezing of the solvent is a well known phenomenon, as is demonstrated in ice cubes one can make in a household refrigerator. In such an ice cube, it can be seen that the bulk of the cube is transparent, i.e., it consists of water that it free of all macroscopic and microscopic particles, while the center of the cube is opaque. This is due to the fact that almost all of the solute, be it solid, like dissolved metals, or dissolved gases, e.g. air, are concentrated at the center. This occurs because the lowering of temperature of the water lowers the solubility of most solutes in water, thus forcing out the solutes from the liquid phase. Thus it can be reasonably concluded that the solute concentration is driven ahead of the freezing front. This fact was the basis for the design of the experiments to prove the efficacy of a process to remove contaminants from water.

Freeze concentration was first implemented by Shapiro in 1961, when he applied freezing as a means of concentrating organic compounds (Lorain *et al.*, 2001). Later in 1964, Kobayashi and Lee concentrated rhodamine B and sodium Chloride by the same method. Baker in 1967 – 1970 did important work in using freezing to improve detection of organic compounds like phenol, alcohol and acid.

The basic principle of freeze concentration is given by Lorain *et al.*, 2001, using a solid-liquid phase diagram shown in Fig – 2.7.

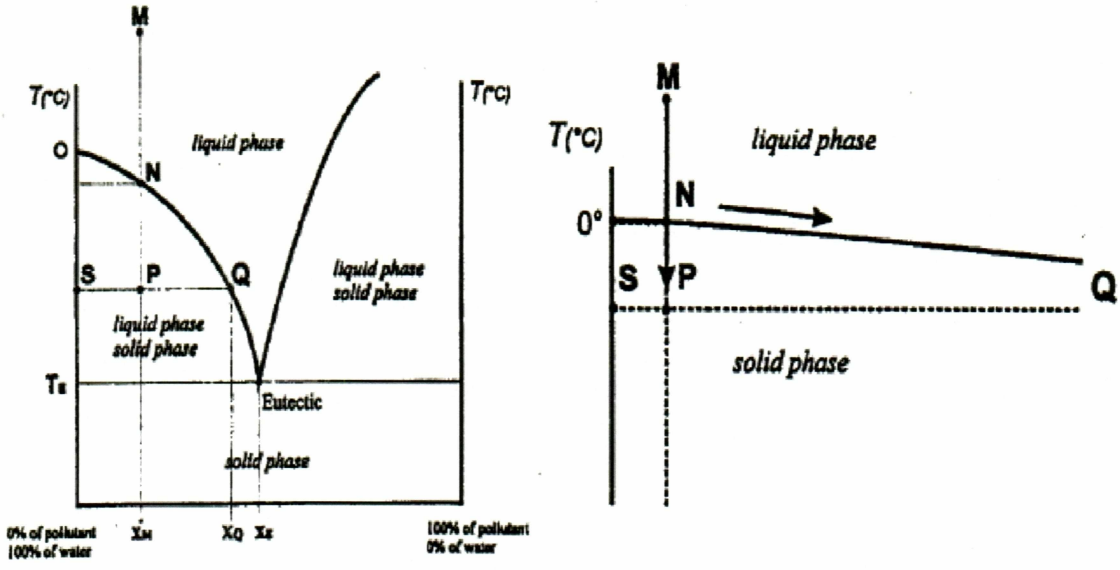

Fig – 2.7: Solid-Liquid Phase Diagram for Eutectic Separation (Lorain *et al.*, 2001)

In the diagram on the left hand side, a solution of an arbitrary pollutant X in water is considered. The vertical coordinate of point M is the temperature from which the freezing process is begun. The horizontal coordinate gives the percentage of pollutant X by weight in unit quantity of water. Thus point M also signifies the percentage of pollutant X in water when the freezing process was begun, and is represented by x_M in the figure. The freezing process is conducted until the temperature at point P is reached. We see that the line MP intersects the curve at point N, which is the point where ice crystals are obtained for the first time. As shown in the figure, point P lies in the liquid phase + solid phase area. This signifies that a portion of the water will freeze to ice, while all of the pollutant X in the solution will be driven into the liquid water that still exists under that condition of temperature and pressure. Thus the concentration of X in the leftover water is increased, and is denoted by point x_Q. The proportion of solid ice in the mixture is given according to the inverse segments method by the ratio PQ/SQ, and the proportion of liquid is given similarly by the ratio SP/SQ. It is important to note at this point that the ice generated is pure and free from all included pollutants. This is mainly due to the small size of ice lattice crystals, making inclusion of a pollutant all but impossible. The eutectic temperature for the

solution is the physical limit of the process, as at that temperature co-precipitation of ice and pollutant X will occur, making separation impossible.

Lorain *et al* note that wastewater may be considered to be of low concentration in dissolved matter, as the horizontal axis denoting concentration is expressed in terms of percentage weight of salt in the solution, thus never exceeding a few grams per liter. Therefore the initial concentration denoted by point M in Fig 2.7 will be very close to the vertical axis, as noted in the diagram on the right hand side of Fig 2.7. As a result, even with a temperature of a few degrees below zero, significant separation can be achieved. The authors also noted that while a solution with a single solute (contaminant) may be easy to analyze, multi-solute systems are much more complex and very difficult to control or analyze. This investigation, however, does not take into account the important point that the degree of purification of water is dependent on the speed with which the ice front advances into the liquid phase, i.e., the rate of freezing and the effect of stirring the ice/liquid interface to prevent a concentration of solute on the interface.

Miyawaki *et al.* (1998) conducted an investigation of the effective partition constant of the solute between ice and liquid phases in a concentrate glucose model. The effective partition constant K can be defined as follows.

$$K = C_S/C_L \qquad \text{(eq. 8)}$$

Where C_S and C_L are the weight percentages of the solute in ice (solid) and liquid phases respectively.
As C_S decreases, the value of K also decreases, thus a low value of K is desirable. The authors have derived a theoretical expression for K, which is as follows.

$$K = K_0/[K_0 + (1 - K_0)\exp(-u/k)] \qquad \text{(eq. 9)}$$

Where,

K_0 is the intrinsic partition constant defined as

$$K_0 = C_S/C_i \qquad \text{(eq. 10)}$$

Where C_S and C_i are the percentage weight concentrations in the solid ice phase and

the initial concentration in the liquid phase respectively.

u is the speed at which the ice phase grows into the liquid phase.

k is the mass transfer coefficient at the boundary layer between ice and water.

k is found to have a relation with the rate of stirring, which is expressed as

$$k = aN^b \qquad \text{(eq. 11)}$$

Where N is the r.p.m. of the stirring motor, and a and b are experimentally determined constants.

We can see from eq. 9 and eq. 11 that as the r.p.m., N, increases and the speed of the freezing front, u, decreases, the value of K decreases. Thus is can be said that for effective freeze separation, a high rate of stirring and a low rate of freezing are required.

The theory of freeze concentration has been implemented successfully in many laboratory scale experiments.

Gay *et al.* (2003) purified artificially contaminated water by radial freezing with stirring. The water contained about 2 gm/kg of clay and either zinc (656 – 701 ppm) or lead (2116 – 2230 ppm). As lead and zinc were both introduced as nitrates, nitrate concentration in the solution was 1186 – 1536 ppm. The freezing was conducted at -4 °C to -8 °C. The inner rotating steel cylinder was cooled by a 30% glycerol solution. The outer Plexiglas solution remained fixed. The freezing front propagated from the inner to the outer cylinder. The inner cylinder was rotated at 120 r.p.m. While sampling, the inner cylinder was gently pulled away with the purified ice, whereupon the ice was melted and analyzed. The same experiment was also repeated without

rotating the drum, i.e., without stirring. Table 2.3 gives the results for the experiments with stirring.

Table 2.4: Results for Freeze Concentration with Stirring (Gay *et al.* ; 2003)

pH	Heavy Metal	Initial Concentration (mg/l)		Final Concentrations (mg/l)		Purification Rates	
		Metal	Nitrate	Metal	Nitrate	Metal	Nitrate
5.0	Zinc	664	1536	8.2	27	98.77	98.24
6.0	Zinc	656	1419	3.8	16.4	99.42	98.84
7.5	Zinc	677	1231	0.2	2.7	99.97	99.78
8.0	Zinc	687	1241	0.3	1.8	99.96	99.86
8.5	Zinc	683	1236	0.2	0.4	99.97	99.96
10.0	Zinc	701	1250	0.2	5.3	99.97	99.57
5.0	Lead	2116	1219	9.6	9.3	99.55	99.24
6.1	Lead	2118	1209	1.6	4.9	99.92	99.60
7.5	Lead	2230	1256	0.7	7.1	99.97	99.44
9.0	Lead	2158	1269	3.0	15.9	99.86	98.74
10.2	Lead	2158	1186	0.8	6.2	99.48	99.48

It can be seen that in all cases a very high percentage of separation of metals is achieved. It is also noted by the authors that in the absence of stirring, the removal efficiency drops drastically.

Another novel method using freeze concentration, the use of hydraulic refrigerant compressors, has been described by Rice and Chau (1997). This system has been widely used in desalination of seawater. A diagrammatic description of the process is given in Fig – 2.8.

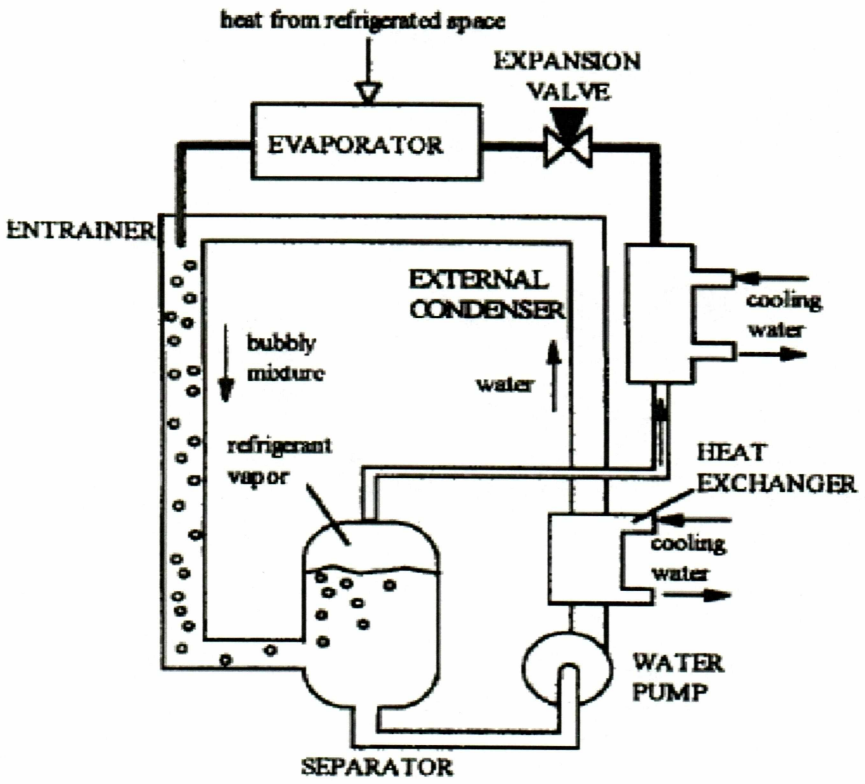

Fig – 2.8: Representation of Hydraulic Refrigerant Compressor (Rice and Chau, 1997)

In the system, a low pressure refrigerant enters the water column from the Evaporator through the Entrainer at the top of the column. The flow of contaminated water in the column is downwards. The refrigerant, in the gaseous phase, is bubbled through the water, and is carried down along with the flow. On the way down, the bubbles are compressed by the weight of the superincumbent water, and the refrigerant liquefies. The mixture is them transferred to the separator, where the pressure is much lower. The liquid refrigerant bubbles immediately vaporize, taking the latent heat of vaporization from the surrounding water, thus turning some water to ice. These ice crystals are mostly free from the dissolved contaminants and can be separated out and remelted to form purified water. The escaped refrigerant vapor can be recirculated and reused. The advantages of the process are low energy costs, as evaporation, condensation and refrigeration can be run complementary to each other thus circulating the energy within system. Also the system has few moving parts and is not

prone to wear and tear. n-butane is preferably used as a refrigerant, as it is cheap and environmentally friendly. A primary problem with this technology, however, is designing and constructing equipment of appropriate size. Separation of ice from the unfrozen brine and remelting it can also be problematic.

Freeze concentration can therefore be used, in theory and practice, to decontaminate water effectively and cheaply.

2.4 Literature Review on Reverse Osmosis

Reverse osmosis and ultrafiltration are very efficient processes for removing contaminants from water. The principle of reverse osmosis can be explained in the following way.

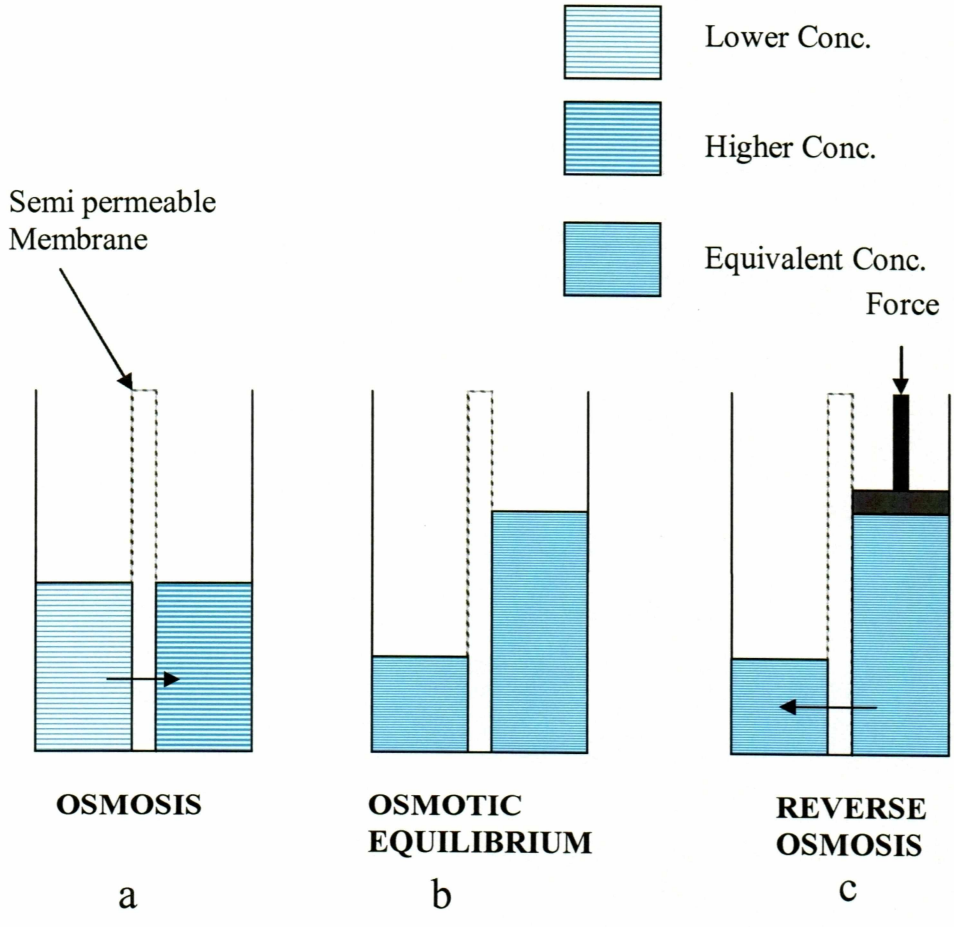

Fig – 2.9: Reverse Osmosis Principle

In Fig 2.9(a) and 2.9(b), the process of osmosis is explained. Fig 2.9(a) shows a container divided by a semipermeable membrane. Semipermeability in this case would require that the membrane allow only the solvent to pass through and not the solute. In Fig 2.9(a), the chamber on the left hand side contains a lower concentration of solute and has a lighter shade of blue, while the chamber on the right hand side contains a solution with a higher concentration of the same solute, and has a darker shade. In such a situation, the action of osmotic pressure will propel the fluid from the lower concentration chamber to the higher concentration chamber until the two concentrations are equal, as shown in Fig 2.9(b). Reverse osmosis is said to occur if, by some mechanical force, the flow due to osmosis is reversed, as shown in Fig 2.9(c). In such a case, water will flow from the right hand side to the left hand side chamber, thus diluting the concentration of the solute there, and producing purer and purer water.

The effectiveness of reverse osmosis in removing contaminants from water is amply demonstrated. Abu Qudais and Moussa (2004) treated artificially contaminated water with Cu^{2+} and Cd^{2+} ions, and achieved 98% and 99% removal for copper and cadmium respectively. In a multiple ion situation, the membranes were found to reduce a 500 ppm solution to 3 ppm.

Afonso *et al.* (2004) investigated the technical and economic feasibility of desalination of brackish water in Jordan. The membranes gave a water recovery ratio of 77.5%, and 98% of the organic and inorganic matter present in the raw water was rejected. The cost for water production was 0.26 €/ m^3, which was deemed by the authors to be affordable.

Bodalo-Santoyo *et al.* (2004) found that removal of ammonia and sulphide ions from solution can be achieved to a high percentage, but is dependant on the influent pH.

Peng and Escobar (2003) developed mathematical models for the rejection efficiency of different substances that affect the quality of water. Synthetic raw water with different concentrations of organic carbon, in the form of humic acid and dissolved organic carbon (DOC) and different hardness as $CaCO_3$ equivalent was prepared. The

pH was adjusted to 7 using 0.1 M NaOH. The test was conducted on three separate membranes, after which the results were statistically tested to determine their statistical significance. A flat sheet test apparatus with a effective membrane area of 155 cm^2 was used.

The model for Turbidity Rejection, for example, was found to be a function of the turbidity in Raw water, the membrane zeta potential, specific ultraviolet absorbance in raw water, ultraviolet absorbance at 253.7 nm (UV_{254}) in raw water and the molecular weight cut off.

This model and all the other models were found to be statistically significant. These models were developed using particular membranes with particular temperature and pressure. While they do provide a way to evaluate membrane performance with fewer experiments, the equations may not be universal, and even the membranes used in the study might react differently to a different set of water quality parameters. This model was not used in this thesis to evaluate membrane performance, as many of the parameters used in the models were beyond the scope of current research.

The biggest drawback of this technology is membrane fouling, which, according to Lepore and Ahlert (1998) is the "most formidable" obstacle to a wide implementation of reverse osmosis. Fouling manifests itself by a reduced throughput and a drop in the quality of the effluent produced. The authors state that to prevent fowling, several steps may be taken, including avoiding steel in favor of plastic as manufacturing material, controlling pH, a wide range of pretreatment options like filtration of large particles, converting some compounds such as CaCO3 to a more soluble form, removal of scaling compounds, not allowing bacterial growth, and finally regular backflushing to clean the membrane.

CHAPTER III
EXPERIMENTAL PROCEDURES

3.1 Introduction

This chapter deals with experimental procedures that were employed to arrive at conclusions about the effectiveness of the three techniques that are being investigated, viz., bioremediation, freeze concentration and reverse osmosis. The experiments were conducted at laboratory scale at first. In the case of bioremediation, a pilot scale model was set up and analyzed whereas no such model was used in the cases of freeze concentration or reverse osmosis. All the details of the design and setup of the experiments, collection and preservation of the samples and their analysis are presented in this chapter.

3.2 Experimental Procedures for Bioremediation

The laboratory scale experiments were conducted indoors at room temperature (20° C approx.) and ambient pressure. At the outset it was decided that sample water from a mine would be used for the experiments as much as possible, so that experiments would be as close to the conditions in a mine as possible. The biomass used to kick-start the chemical reaction to produce sulphate reducing bacteria was initially chosen to be bovine manure, and later garden compost from the Fairbanks area was used. The introduction of mine water samples and garden compost presented two obvious problems to the design of the experiments. Both these components are fairly variable in composition and do not have a constant chemical composition. It was felt that the veracity of the fact that metals can be removed from of solution using bioremediation in this particular case, i.e., with these particular samples of mine water and compost, needed to be established first. In order to do this a set of tests were run to prove the principle.

3.2.1 Proof of Principle Test

The proof of principle consisted of 20 gm of biomass being put into a jar and 125 ml of mine water being added to it. The jar was then sealed and was left undisturbed for

seven days. Five replicates were run for the entire setup. Bovine manure was used as the biomass. The concentrations of four target metals in water, lead, zinc, cadmium and iron, were tested using a Perkin-Elmer Atomic Absorption Spectrophotometer. In the initial stages, the analysis of a fifth target metal, manganese, was not done because of equipment limitations. The analyses of samples at this stage were inconclusive, i.e., there was no significant difference between the concentrations of the metals in the mine water being used in the experiments and the "treated" water after one week. This failure was deemed to be due to the fact that the bovine manure was collected fresh and was then frozen, thus allowing no time for the bacteria to colonize the biomass. From this set of experiments onwards, the biomass was changed to Fairbanks area garden compost. This factor was maintained as a constant throughout the remainder of the experiments.

The next set of experiments was conducted as is shown in Fig –3.1. As the first set of experiments had failed to prove the principle of bioremediation using the bovine manure and actual mine water, a second attempt was made to prove the principle of bioremediation. This was done by creating water contaminated with lead (4.6 ppm), and using Fairbanks area garden compost as the biomass. A four liter plastic vessel was used in the experiment. An unspecified amount of biomass was put in it. The biomass was not weighed at this point as the focus of the exercise was qualitative and not quantitative. The compost was then compacted, and was held down by metal free rocks. Two liters of the contaminated water were placed in the vessel, and the setup was left undisturbed for one week.

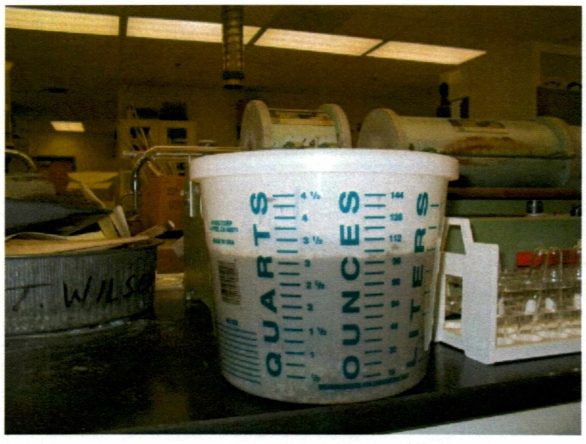

Fig – 3.1: Bioremediation Proof of Principle

The effluent after one week was tested for concentration of lead using the Atomic Absorption Spectrophotometer. By the flame method, lead concentration was found to be lower than the detection limit on the machine. This experiment was then deemed to have proved that the idea of bioremediation works in principle.

3.2.2 Repeatability Analysis

Efforts were then directed toward understanding the process of bioremediation, as happening in this case. It was decided that repeatability analysis would be undertaken. To this end, artificially doped solutions were used. As before, manganese determinations were not made as due to analytical limitations. The concentrations for the other four metals in the influent solution were as follows: - lead – 80 ppm, zinc – 129 ppm, iron – 35 ppm and cadmium – 91 ppm. The setup was as shown in Figure 3.2.

In this case a similar setup to that used with the bovine manure was used. Eight ounce mason jars were loaded with 20 gm of compost and 125 ml of contaminated water and left undisturbed for one week.

Fig – 3.2: Repeatability Analysis

Each metal was replicated twice. In all the cases it was found that the metal concentration was reduced to a level not detectable by the Flame Atomic Absorption method. It was determined that the biomass being used in the experiments was capable of reducing metal concentration in contaminated water to below detection limits of the A-A apparatus.

At this stage the decision was made to change the primary method of analysis from Atomic Absorption Spectrophotometer to the Inductively Coupled Plasma – Mass Spectrometer (ICPMS). This decision was taken for two reasons. Firstly, the Atomic Absorption unit was not equipped for manganese detection. Secondly in case of the metals lead, zinc, cadmium and iron, it was found that the effluent water had a very high concentration of dissolved organic substances, which could act as a depressant for the signal received by the sensor in the A-A apparatus, thus giving an inaccurate reading for the metal concentration. The ICPMS, which works at a temperature of

6000 – 7000° F, would dissociate and disintegrate all organic molecules, thus providing a clear signal and an accurate reading.

3.2.3 Field Scale Experiments

It was then decided to employ bioremediation in a set of field scale experiments that would provide a measure for its performance under non-ideal conditions. The Teck-Cominco Red Dog mine (see Fig 2.2) allowed the use of its facility for this set of experiments. Figures 3.3, 3.4 & 3.5 depict the field bioreactors that were set up.

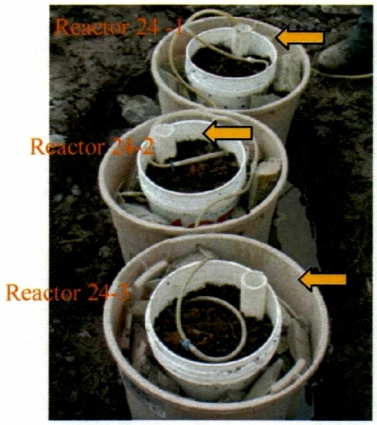

Fig – 3.3:
Reactor Site 24

Fig – 3.4:
Reactor Site 23 - PFR

Fig – 3.5:
Reactor Site 23

A total of five reactors were established in two separate sites (site 23 and site 24). The sites were selected as they had run off streams from the mine waste dump. The water of the streams was known to be high in dissolved metal content.

- Figure 3.3 shows the first three reactors established at site 24. The reactor design was such that the influent to the reactors would be taken directly from the run off streams and the effluent would be collected from *inside* the reactor from the sample wells indicated by the orange arrows. Two of the reactors (24-2 and 24-3) were inoculated with Fairbanks area garden compost and (24-1) was filled with local peat. The intended residence time for the reactors was seven days.

- Figure 3.4 depicts reactor 23-2 at reactor site 23. Reactor 23-2 was designed as a plug flow reactor (PFR). The reactor was filled with local peat and inclined toward the bucket shown in the picture with a red arrow. The feed was introduced up gradient, which then trickled down through the reactor and into the bucket. The effluent was sampled.
- Figure 3.5 shows reactor 23-1 at reactor site 23. The reactor is a perforated bucket filled with local peat. The green arrow in the picture indicates the general direction of flow of water in the ground in the area. The reactor was placed in the path of the flow so that contaminated water flowed through the perforated bucket, reacting with the biomass, thus purifying the water. Influent samples were taken from the sampling well outside the perforated bucket and effluent samples were taken from the sampling well inside the bucket.

Samples were collected by Red Dog Environmental department personnel and were analyzed at UAF with the help of the ICPMS.

3.2.4 Performance Analysis for Bioremediation

Fig – 3.6: Bioremediation Performance Analysis

The results from the test encouraged us to perform further investigations on bioremediation. The setup used is depicted in Figure 3.6 above. There were five sets of experiments run, targeted to produce data on five different properties.

- Experiment series 1 was run as a replication of the basic bioremediation process, i.e., it was run so that we could again verify that remediation was indeed occurring in the contaminated water if it was left in biomass undisturbed over for a period of time. To this end, each of five eight ounce mason jars (numbered 1-1 to 1-5) were loaded with twenty grams of biomass and approximately 125 ml of mine water and left undisturbed for a period of one week. It is important to note here that the first proof of principle test was conducted with synthetic solutions.
- The experiment series 2 was run to find out the minimum quantity of biomass required lower the concentration of metal from the contaminated mine water. The experiment was designed as follows: - Five mason jars were used (2-1 to 2-5). In all the jars, the quantity of contaminated water was kept at a constant 125 ml. In jar 2-1 the quantity of biomass added was 20 gm, in jar 2-2 16 gm, in jar 2-3 12 gm, in jar 2-4 8 gm and in jar 2-5 4 gm. All the jars were left undisturbed for one week.
- The third set of experiments was the series 2R in which again five jars were used. These were replicates of the series 2, with 2R-1 containing 20 gm of biomass, 2R-2 containing 16 gm etc.
- The fourth set of experiments was the series 3, which were conducted for reusability analysis of the biomass. Here too, five mason jars were used, and the quantity of water and biomass were maintained at 125 ml and 20 gm respectively.
- The fifth set of experiments was conducted to ascertain the residence time of the water in these mini-reactors with standardized conditions. The set was labeled 4-1, 4-2,..., 4-6. The quantity of water and biomass were left constant at 125 ml and 20 gm. 4-1 was left undisturbed for seven days, 4-2 for 6 days etc., and finally 4-6 was left in place only for one day. Thus on the seventh day of the experiment, all the experimental jars were unsealed and their contents sampled.

Before the experiment series 1, 2, 2R, 3 and 4 were set up, baseline analysis was performed to determine the metal concentrations of the influent water, which was

lead-zinc concentration plant water from the Red Dog mine. The results are tabulated in Table 3.1.

Table 3.1: Influent concentrations in ppm for experiments series 1 – 5.

Metal	Concentration in ppm
Lead	56.7
Zinc	4259.8
Cadmium	322.6
Iron	1020.49
Manganese	77.8

3.2.5 Sorption Experiments

It is recognized that the two principal processes of metal removal in bioremediation are bacterial remediation and sorption, sorption being the quicker of the two reactions. Sorption experiments were conducted in order to determine the percentage of metals removed by the sorption process, as opposed to the bacterial remediation process. The experiments were conducted in five mason jars. Each eight ounce jar was loaded with 20 grams of compost and 125 ml of Red Dog Mine water. The mine water had been left standing in a sealed bucket between the times the performance analysis and the sorption experiments were conducted, and had changed in composition. The jars were then left on a shaker table for three hours, whereupon the effluents in the jars were analyzed for metal content by the ICP-MS. The results for this experiment are discussed in Chapter IV.

3.2.6 Digestion Experiments

Digestion experiments were conducted to determine whether there was a difference in metal content in the compost being used for bioremediation before and after the bioremediation reaction. For this set of experiments biomass from the experiments 1-1 through 1-5 (already described in section 3.2.4) were used. The solid phase from each individual jar (1-1 through 1-5) along with an unreacted sample of biomass were

dried and homogenized. An aliquot of 125 mg was taken from each sample of biomass, which was then digested using the apple leaf digestion procedure. The aliquots were treated with one liter 70% HNO_3, 200 ml of concentrated H_2SO_4 and 400 ml 60% $HClO_4$. This mixture was then boiled first at 300 °C for 15 minutes and then at 600 °C for 45 minutes. The metal content of the digested samples was determined using the ICP-MS. The metal precipitates were not separated from the biomass.

3.3 Experimental Procedures for Freeze Concentration

While designing freeze concentration experiments, it was noted that in a place like Alaska, where temperature may stay very low for most of the year thus facilitating freezing, freeze concentration might emerge as a cost effective method for separating contaminants from water. Thus, the way in which an industry might implement the procedure was taken into consideration so that the experiments could simulate applicable conditions as closely as possible.

3.3.1 Experiments with Radial Freezing

The first model considered was the water freezing radially inwards in a cylindrical container. It was surmised that an industry might choose to place the contaminated water out in the open in cold weather in drums or pipe with insulation on the ends so that the primary front of freezing moves radially inward. This would concentrate the contaminants along the longitudinal central axis of the drum. Separation of contaminants can then be achieved by any suitable means, e.g., coring the center out with a drill. The concept is illustrated in Figure 3.7.

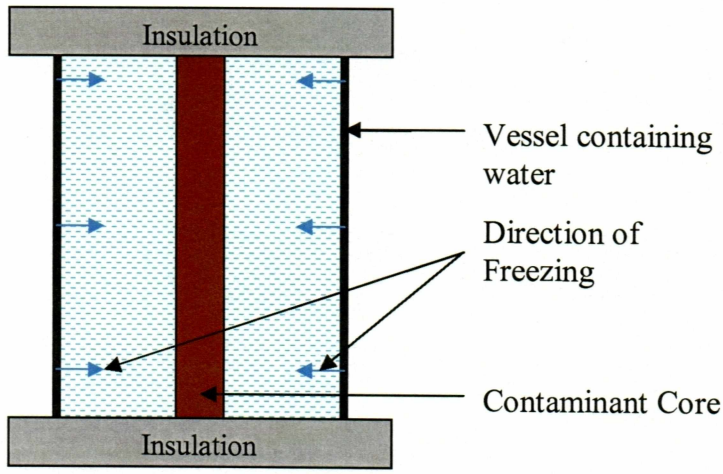

Fig – 3.7: Illustrated Longitudinal Section of Radial Freezing Experiments.

In the initial set of experiments, cardboard tubes coated with paraffin wax were chosen as the vessels to freeze the water in. The water used was mine water from the Teck-Cominco Red Dog mine and the Kennecott Greens Creek Mine. The cardboard cylinders proved susceptible to leaking and soaking in spite of the paraffin coating.

The cardboard tubes were replaced with plastic pill bottles. The contaminated water used in this set of experiment was deionized water artificially doped with contaminants. At this stage samples for only four metals were prepared, as the wherewithal for analysis of manganese was not present. The temperatures at which the water samples were frozen and the concentrations of the four target metals in the influent water are given in Table 3.2.

Table 3.2 : The Influent Concentrations and Temperatures for Freeze Front Tests

Sample Designation	Temp. Frozen (C)	Metal	Concentration (Influent) ppm
Pb - 1	-10	Pb	80
Zn - 1	-10	Zn	129
Fe - 1	-10	Fe	35
Cd - 1	-10	Cd	91
Pb - 2	-20	Pb	80
Zn - 2	-20	Zn	129
Fe - 2	-20	Fe	35
Cd - 2	-20	Cd	91

The samples were then cored out at the center with a 5/8″ drill bit using a standard drill press. The cores were then melted down and analyzed. The results, which are discussed in Chapter IV, gave us very high concentrations of the four metals under analysis. It was surmised that the drill bit, which was previously used to drill metal, was responsible for contributing excess metal to the drilled cores. Also, this design was deemed impractical for industrial application.

3.3.2 Experiments with Top Down Freezing

The second model considered was that of top down freezing. It was surmised that a mining company in Alaska might use their tailings pond as an in situ freezing vessel during the colder months of the year. In most mines in Alaska, the tailings pond, which is the primary repository for contaminated water emanating from the mining and beneficiation operations, remains frozen for the greater part of the year. At fall, when the water is in the process of being frozen, the surface of the pond is exposed to cold atmosphere. In contrast, at the bottom or the sides the water is in contact with either local soil or any lining material that may be placed there. These are normally heat insulators, and though the temperature may be very cold, water at the bottom and the sides will lose heat less effectively than that at the exposed surface. Therefore, though freezing will occur from all sides, the freezing front from the top down will

gain dominance, effectively concentrating the contaminants toward the bottom of the pond. The mine could use mechanical means to dig out or dredge out the ice at the top, thus collecting relatively purified water and dumping it separately, while they wait for the spring thaw to melt the lower portions of the frozen pond in order to treat the concentrated water.

In order to simulate the process small plastic containers were chosen as the freezing vessel. The vessels had a larger cross sectional area at the top than at the bottom and were of two shapes, square (141 mm x 141 mm x 47 mm) and rectangular (210 mm x 139 mm x 56 mm). Red dog mine plant water was poured into these containers. The bottoms were insulated with thermal insulator material, and the sides were wrapped with paper. They were then placed outside in open air in a protective box. The ambient temperature outside on that day was -38 °C. Lids were placed on top but were left loose to allow for expansion of the ice. The setup is represented in Figure 3.8.

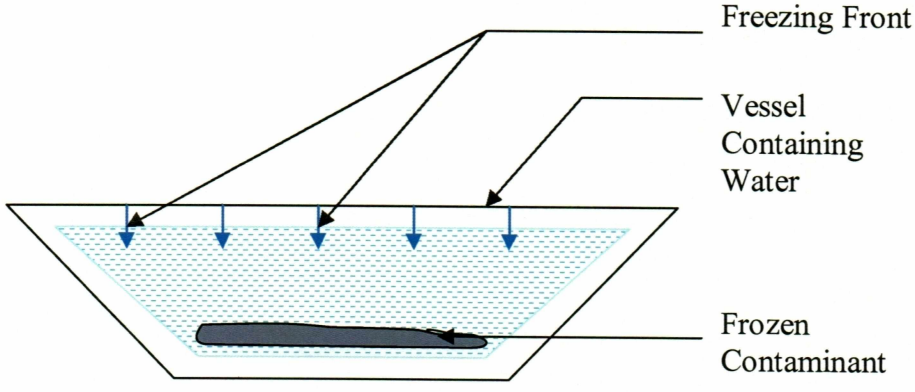

Fig – 3.8: Illustrated Longitudinal Section of Top Down Freezing Experiments

After freezing, samples of ice were collected by drilling out a depth of about 10 mm from the top and bottom of the frozen slab using a 1-1/2″ winged bit. Two holes were drilled on the square frozen slabs, one on the top and another on the bottom. Four holes were drilled on the rectangular slabs, two on the top and two on the bottom.

The experiment was repeated by freezing at – 15 °C. The results are discussed in Chapter IV.

3.4 Experimental Procedures for Reverse Osmosis

Reverse osmosis is an efficient, albeit expensive method for removing contaminants from water. It uses osmotic membranes to create a barrier between pure and contaminated solvent, in this case water, then employs mechanical pressure to overcome the osmotic pressure to propel the water from the contaminated compartment to the pure one while restraining the contaminating solutes.

In order to conduct experiments of reverse osmosis, a bench scale reverse osmosis unit was purchased from G.E – Osmonics Inc., Vista, Ca, along with several membranes of different specifications, and pressure chambers for conducting the test. The unit also contains a head tank to hold the fluid being circulated.

This test was conducted using Red Dog mine plant water. The water was diluted using a deionized water to mine water in the ratio 9 to 1. Permeate samples were collected and analyzed by the ICP-MS.

Two types of membranes were used, ADF and DK. ADF is a reverse osmosis desalination membrane, which is rated as being able to reject 99.5% average NaCl, based on 32,000 mg/L NaCl feed at 800 psig net pressure (5,516 kPa) and 77°F (25°C). ADF is used mainly for desalinating seawater. Its optimum rejection pH is 6.5-7.5, operating range 4.0-11.0, and cleaning range 2.0-11.5. DK is a thin-film nanofiltration membrane, which is rated as being able to reject 98 % $MgSO_4$ based on a 2,000 mg/L MgSO4 solution at 100 psig (690 kPa) net pressure, 77°F (25°C). It can operate between pH 2 and 11, and can be cleaned between pH 1 and 11.5.

Flat membranes were used in the initial test. The membranes were placed in the square pressure chambers with an effective area of 80.12 sq. cm. A plain, porous linen cloth was placed between the membrane and the bottom half of the pressure

chamber so that the pressure incident on the filtration surface did not flatten and damage it. The surface was also wetted with a solution of 95 % methanol + 5 % ethanol, so as to maintain the activity of the surface. Before processing samples, deionized water was run through the entire system to flush and stabilize the system. Then the deionized water was bled out and replaced by the diluted mine water. Samples of permeate were collected. Flow rate of the permeate was determined using a graduated cylinder and a stopwatch.

The experiment was repeated with a spiral membrane. The membrane was of the AD class, with an effective filtration area of 3.5 sq. ft. In this case, diluted mine water (9 parts deionized water to 1 part mine water), as well as raw (undiluted) mine water, was passed through the membrane. The results for the experiments are discussed in Chapter IV.

CHAPTER IV
RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter contains the plotted and tabulated results of the experiments described in Chapter III. At the end of enumerating the results for a particular method e.g., Bioremediation, the results are discussed in detail.

4.2 Bioremediation

4.2.1 Results for the Proof of Principle Test and the Repeatability Test

The proof of principle and repeatability tests are described in 3.2.1 and 3.2.2. It has been stated that the metal concentrations obtained from these tests are below the detection limit of the Atomic Absorption apparatus. This indicates that bioremediation has worked in both the cases.

4.2.2 Results for Field Scale Experiments

The tables below (4.1 – 4.5) give the data collected from pilot scale bioremediation experiments. In the tables, the left hand side shaded column indicates the sampling stations in the reactor sites 23 and 24. The rows marked 23–1–Influent, 23–2–Influent and 24–Influent display the concentrations of metals in the influent water to the reactors at sites 23 and 24 respectively. The rows marked 23–1–Effluent and 23–2–Effluent represent the effluent concentrations of metals in the reactor site 23, while those marked 24–1- Effluent, 24–2-Effluent, and 24–3-Effluent represent the effluent concentrations in the reactor site 24. The numbers in the unshaded columns represent the concentrations of both influents and effluents on the dates indicated on the top of the columns. The results for lead, zinc, cadmium, iron and manganese are displayed in Tables 4.1, 4.2, 4.3, 4.4 and 4.5 respectively.

Table 4.1: Lead concentration in ppm in Reactor Influent and Effluent

Sampling Stations	Concentrations in ppm at Dates:		
	8/14/2004	9/2/2004	9/4/2004
24-Influent	25	12	7
24-1-Effluent	15	0.02	0.02
24-2-Effluent	30	0.05	0.02
24-3-Effluent	23	0.03	0.03
23-1-Influent	112	98	218
23-1-Effluent	36	25	245
23-2-Influent	81	4	185
23-2-Effluent	45	19	184

Table 4.2: Zinc concentration in ppm in Reactor Influent and Effluent

Sampling Stations	Concentrations in ppm at Dates:		
	8/14/2004	9/2/2004	9/4/2004
24-Influent	931	4498	3313
24-1-Effluent	182	113	111.2
24-2-Effluent	115	670	500
24-3-Effluent	88	70	59
23-1-Influent	87012	79318	53958
23-1-Effluent	65034	107578	57793
23-2-Influent	24606	94053	150311
23-2-Effluent	134005	116694	72792

Table 4.3: Cadmium concentration in ppm in Reactor Influent and Effluent

Sampling	Concentrations in ppm at Dates:		
Stations	8/14/2004	9/2/2004	9/4/2004
24-Influent	9	412	315
24-1-Effluent	0.90	0.40	3
24-2-Effluent	0.90	37	33
24-3-Effluent	0.10	4	N.D.
23-1-Influent	638	942	633
23-1-Effluent	479	1148	814
23-2-Influent	17935	951	683
23-2-Effluent	456	1046	643

Note: N.D. implies not detected.

Table 4.4: Iron concentration in ppm in Reactor Influent and Effluent

Sampling	Concentrations in ppm at Dates:		
Stations	8/14/2004	9/2/2004	9/4/2004
24-Influent	41	9	345
24-1-Effluent	37	8	0.46
24-2-Effluent	14	186	0.1
24-3-Effluent	31	246	0.3
23-1-Influent	85	165	26
23-1-Effluent	77	471	189
23-2-Influent	2389913*	6192	5468
23-2-Effluent	128593	7389	3314

*Note:- Such values may not be possible and may be results of contamination issues

Table 4.5: Manganese concentration in ppm in Reactor Influent and Effluent

Sampling Stations	Concentrations in ppm at Dates:		
	8/14/2004	9/2/2004	9/4/2004
24-Influent	72	354	283
24-1-Effluent	0.1	59	69
24-2-Effluent	4	165	91
24-3-Effluent	4	87	58
23-1-Influent	8645	9416	6560
23-1-Effluent	8757	13195	9741
23-2-Influent	112533	7099	4813
23-2-Effluent	14259	6136	4395

4.2.3 Results for Bioremediation Performance Experiments

The following Table 4.6 gives the results for the bioremediation replication experiments (experiment series 1 in 3.2.4). The average concentrations and standard deviations are given.

Table 4.6: Effluent Concentrations for Basic Bioremediation Process

Metal	Influent Concentration (ppm)	Effluent Concentration Range (ppm)
Lead	56.7	0.10 - 0.39
Zinc	4259.8	31.45 - 410.54
Cadmium	322.6	0.66 - 2.05
Iron	1020.5	53.09 - 247.88
Manganese	77.8	36.30 - 142.07

The data for Table 4.6 are taken from the analysis of the results of experiments series 1 & 3.

Figures 4.1 through 4.5 depict the data from the experiment series 2 and 2R. Here the X – axis contains the number of grams of compost loaded in the test jars. The highest amount was 20 grams, and it was brought down in steps of 4 grams to the minimum of 4 grams. The Y – axis contains the concentrations in ppm and the Z – axis marks the two replicates.

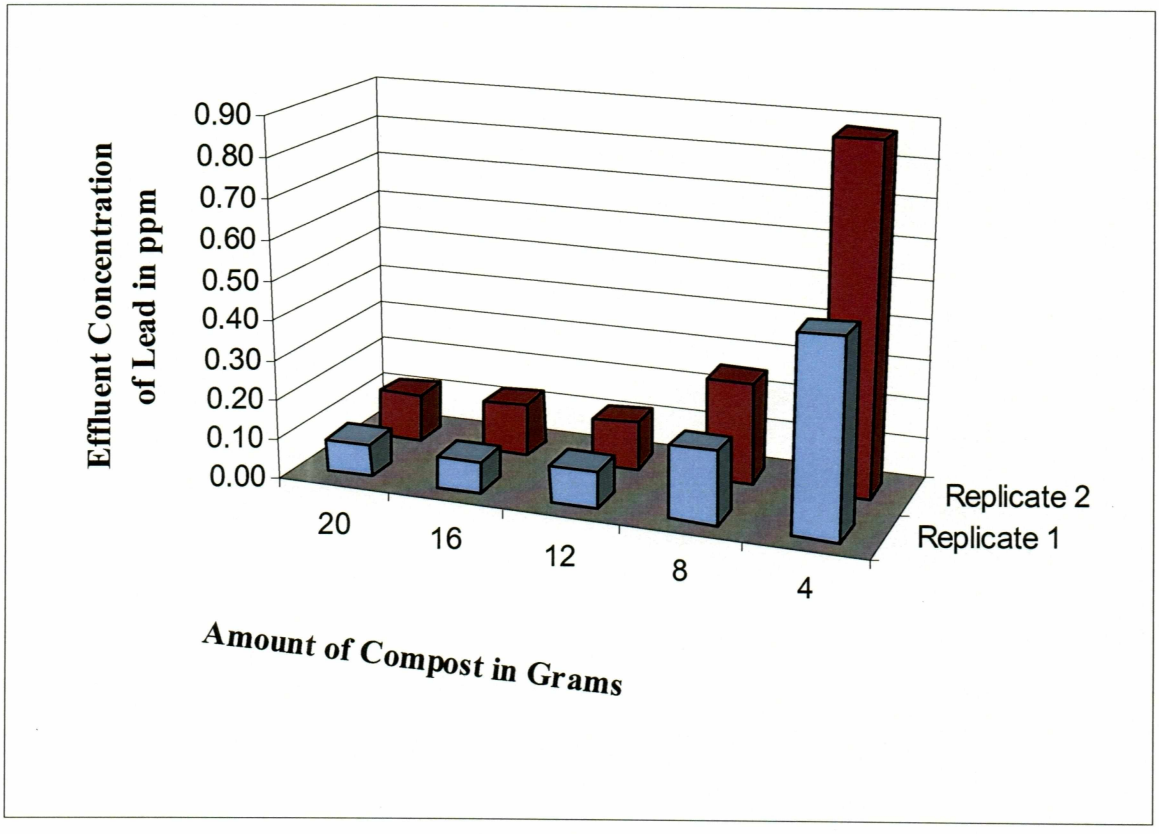

Fig – 4.1: Effect of Quantity of Biomass on Removal of Lead (influent concentration 56.7 ppm)

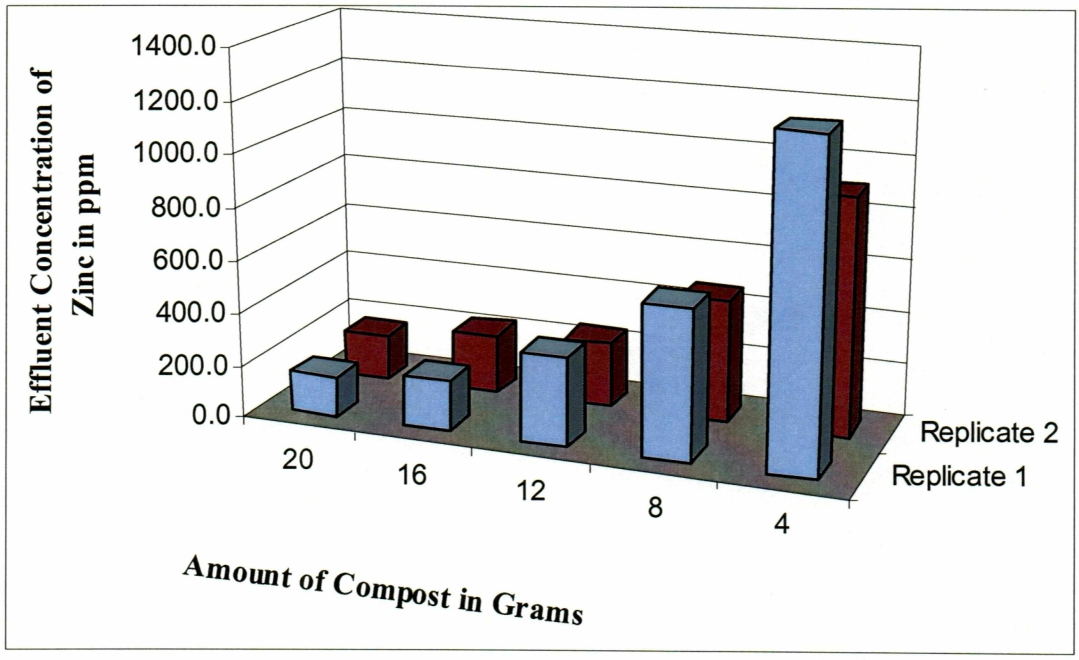

Fig – 4.2: Effect of Quantity of Biomass on Removal of Zinc (influent concentration 4259.8 ppm)

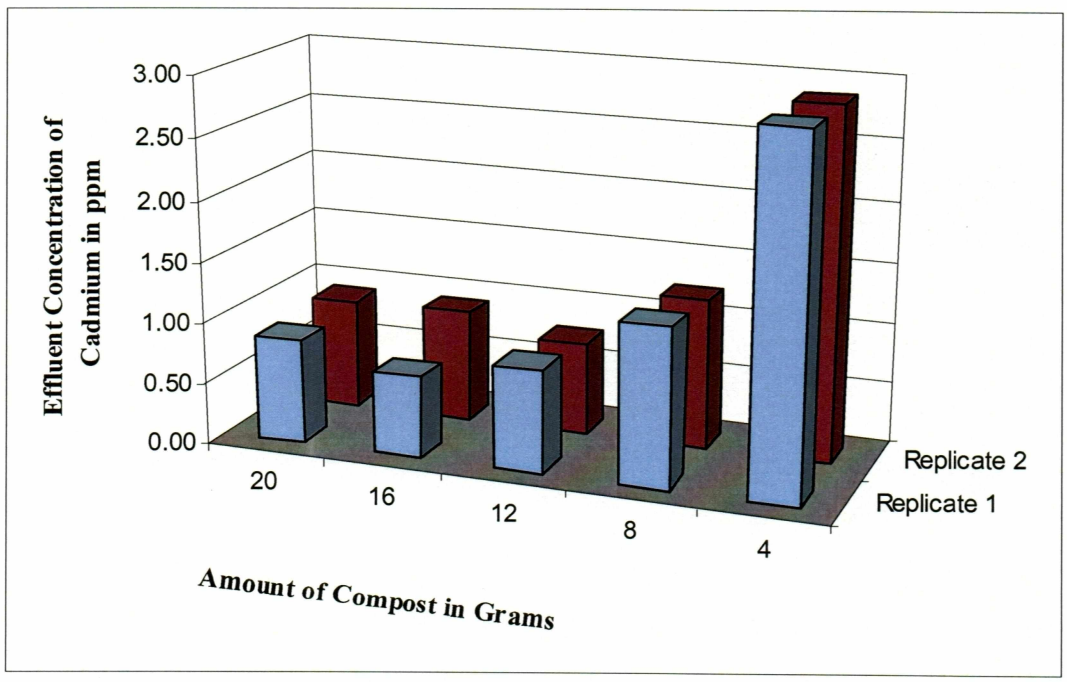

Fig – 4.3: Effect of Quantity of Biomass on Removal of Cadmium (influent concentration 322.6 ppm)

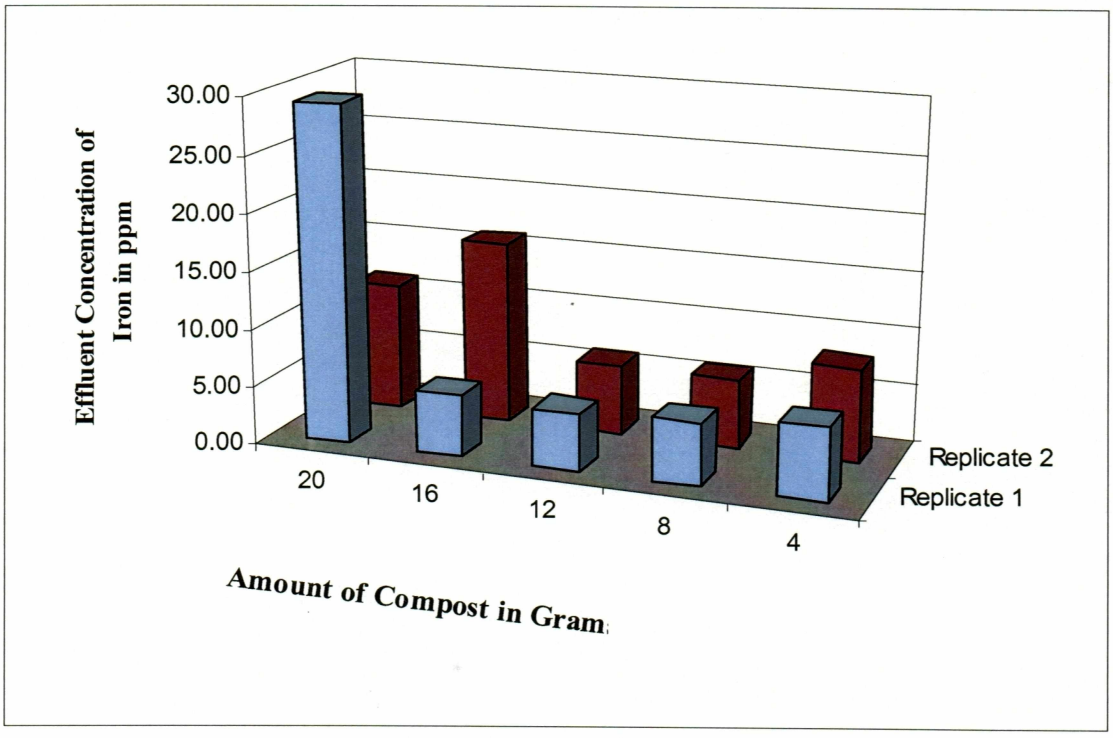

Fig – 4.4: Effect of Quantity of Biomass on Removal of Iron (influent concentration 1020.5 ppm)

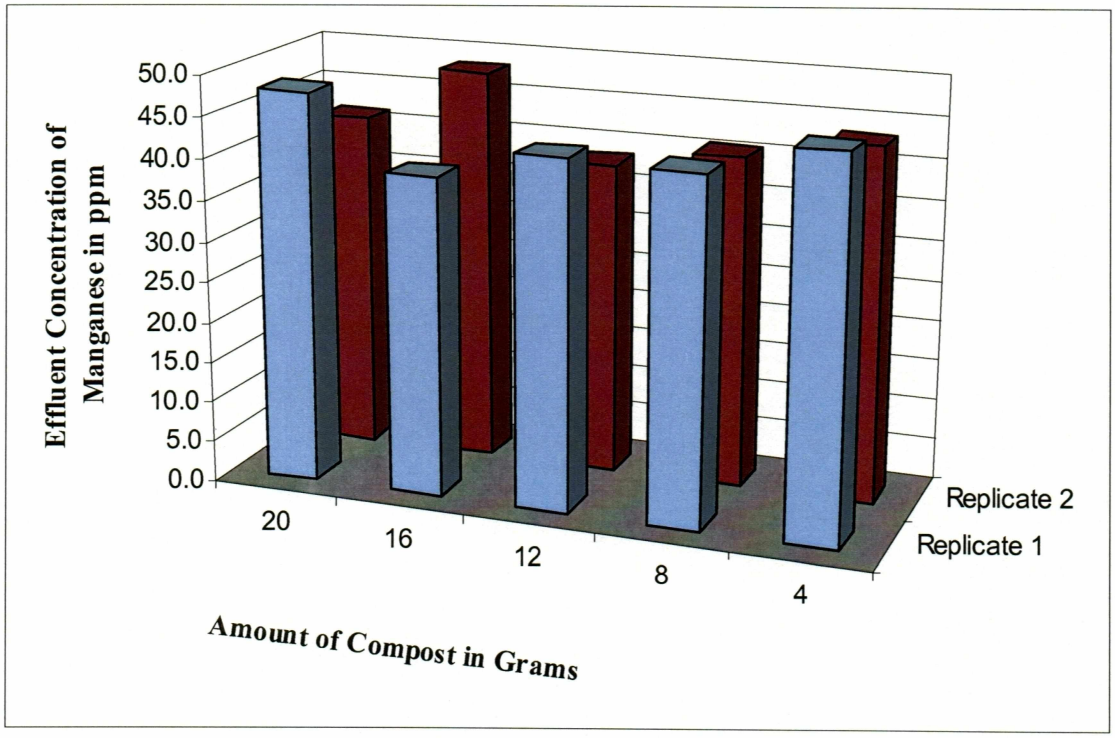

Fig – 4.5: Effect of Quantity of Biomass on Removal of Manganese (influent concentration 77.8 ppm)

The following Figures 4.6 through 4.10 represent the results for the residence time experiments described in the experiment series 4 in 3.2.4. Here the X – axis contains the day number at which the particular experiment was started. The entire set of experiments lasted for a week, and counting down from the seventh day, the experiments were started every day until the last day. Thus the samples on day number 7 were started on day 7, those with number 6 were started on day 6, etc. until the second day. On day number 1 all the samples were unsealed and analyzed. The Y – axis shows the concentrations in ppm.

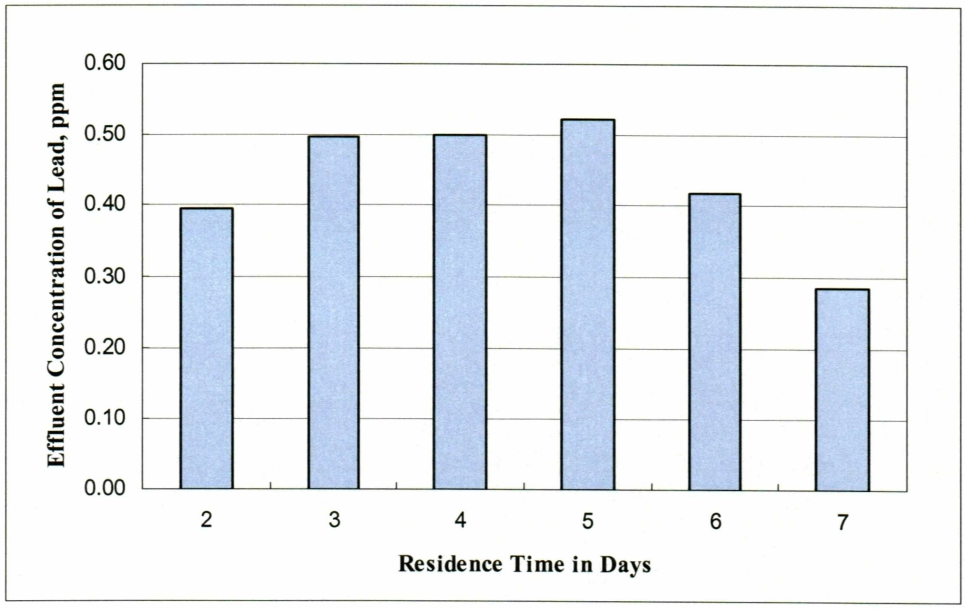

Fig – 4.6: Effect of Residence Time on Removal of Lead (influent conc. 56.7 ppm)

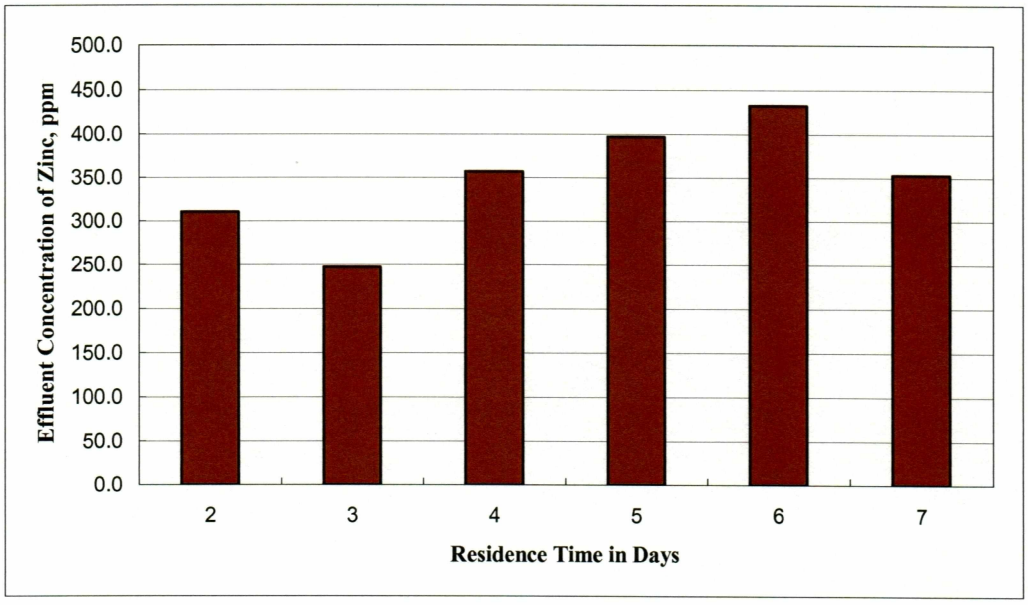

Fig – 4.7: Effect of Residence Time on Removal of Zinc (influent conc. 4259.8 ppm)

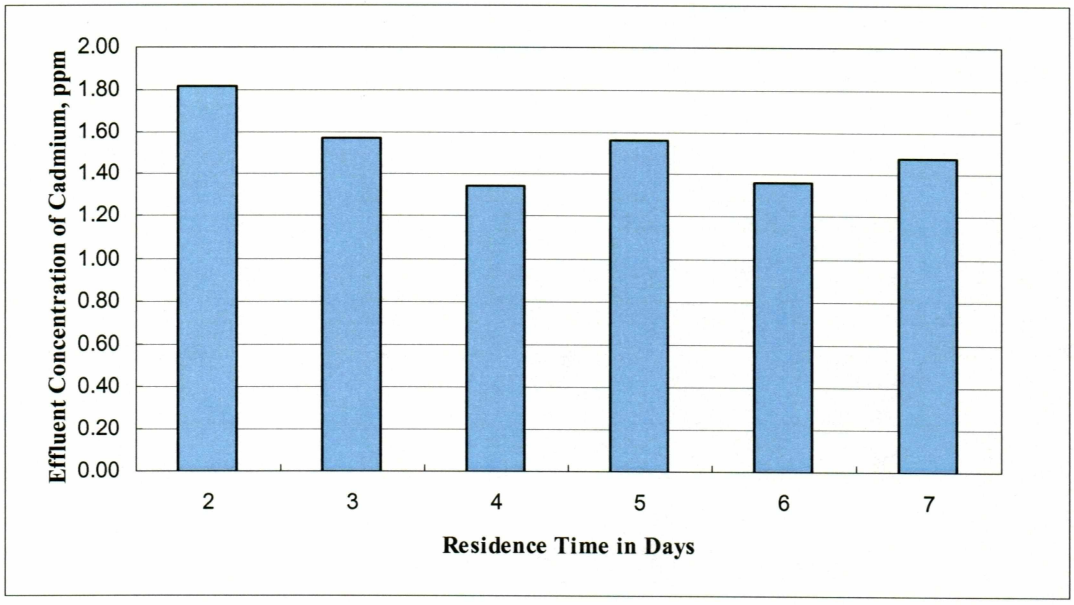

Fig 4.8 : Effect of Residence Time on Removal of Cadmium (influent conc. 322.6 ppm)

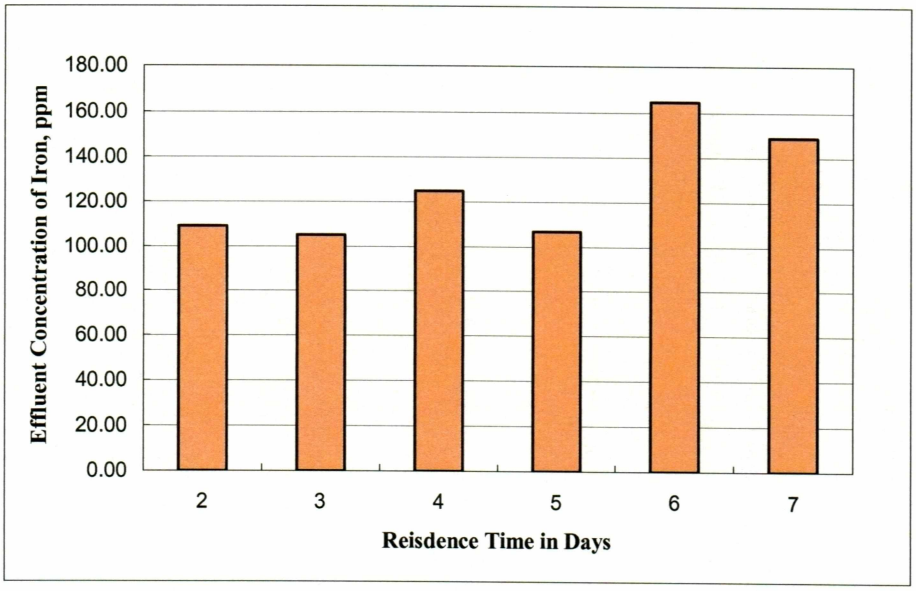

Fig 4.9: Effect of Residence Time on Removal of Iron (influent conc. 1020.5 ppm)

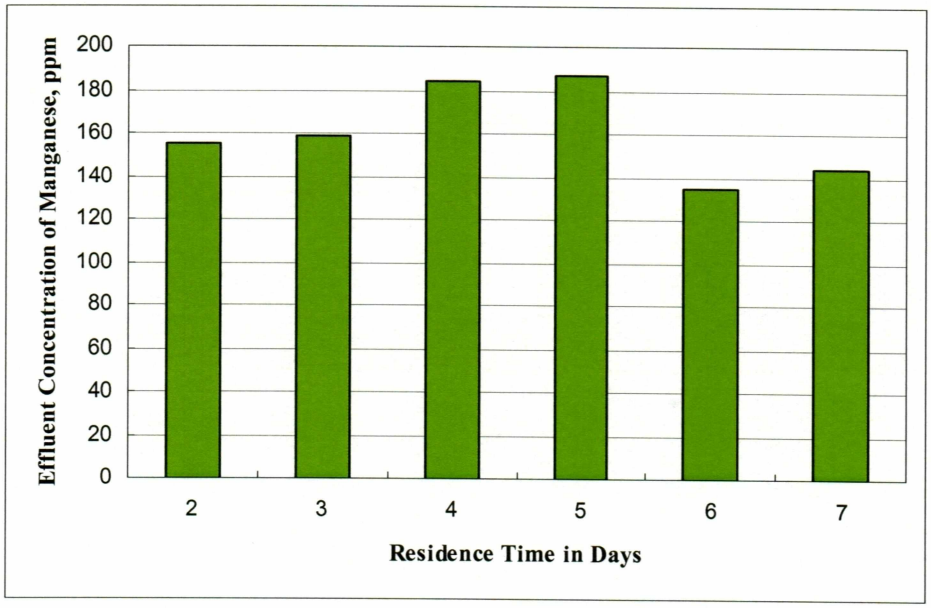

Fig – 4.10: Effect of Residence Time on Removal of Manganese (influent conc. 77.8ppm)

4.2.4 Results for Sorption Experiments

Results for the sorption experiments are displayed in Table 4.7. The first column, shaded grey, displays the sample numbers, the first being the influent concentrations,

followed by the five replicates of the sorption experiment. The remaining unshaded columns give the concentrations of the target metals for each of the five replications.

Table 4.7: Sorption Experiment Results

Sample Numbers	Concentration in ppm of metals				
	Pb	Zn	Cd	Fe	Mn
Influent	4.83	1027.88	1.03	39240.00	21.48
SOR-1	2.43	493.63	0.49	1371.30	20.10
SOR-2	272.45*	446.21	0.45	1063.80	18.21
SOR-3	22.75*	764.52	0.76	1355.50	26.05
SOR-4	0.29	809.66	0.81	2301.20	26.26
SOR-5	5.88	424.82	0.42	1975.10	28.05

*Note: These values are well above the expected levels. It is surmised that these values are due to non-homogenous biomass.

4.2.5 Results for Digestion Experiments

Table 4.8 displays the results for the digestion experiments. The shaded left hand side column provides the sample identification numbers, while the other unshaded columns contain the concentrations of the five target metals for each sample. The first sample, designated "Blank" contains only laboratory grade deionized water. The second sample, designated "2-AL", contains digested apple leaf. Since apple leaf contains very little dissolved heavy metals, this sample provides a good baseline for the remaining data. The third and the fourth samples, designated "3-MB and "4-MB" respectively, are replicates of the digested biomass (compost) that has not been exposed to contaminated water. The remaining samples are digestions of biomass from experiments 1-1 through 1-5, each having been replicated twice.

Table 4.8: Digestion Experiment Results

Sample I.D.	Quantity of Metals in mg per 125 mg compost				
	Pb	Zn	Cd	Fe*	Mn
Blank	0.00	-2.51	0.00	17.72	-0.33
2-AL	0.07	-0.02	0.00	60.25	0.01
3-MB	0.08	0.06	0.00	22770.00	0.22
4-MB	0.03	0.19	0.00	116.50	0.12
5-exp-1-1	0.22	0.29	0.00	12521.25	0.09
6-exp-1-1	0.44	0.31	0.00	7671.75	0.08
7-exp-1-2	0.09	0.30	0.00	6140.25	0.07
8-exp-1-2	0.18	0.26	0.00	9669.75	0.07
9-exp-1-3	0.04	0.32	0.00	12557.25	0.08
10-exp-1-3	0.16	0.32	0.00	8768.25	0.06
11-exp-1-4	81.81*	0.29	0.00	7484.25	0.07
12-exp-1-4	0.07	0.27	0.00	9330.00	0.07
13-exp-1-5	0.18	0.28	0.00	6875.25	0.06
14-exp-1-5	0.20	0.23	0.00	5298.75	0.05

*Note: Some of these values may not be possible. These values may have been the result of contamination during analysis.

4.2.6 Discussion of the Results for Bioremediation

The data for the field experiments in Tables 4 – 1 to 4 – 5 show that the bioreactors in site 24 are working quite well while those at site 23 are much less efficient. Table 4.9 displays the percentage removal of all the five metals by the bioreactors established at site 23 and site 24, Red Dog Mine.

Table 4.9: Percentage Removal of Metals by Bioreactors at sites 23 and 24

Metals	Percentage Removal by Bioreactors				
	24-1	24-2	24-3	23-1	23-2
Lead	65.83	31.67	47.60	28.50	8.15
Zinc	95.35	85.30	97.52	N.R	N.R.
Cadmium	99.42	90.37	99.44	N.R.	89.04
Iron	88.49	49.34	29.80	N.R.	94.20
Manganese	81.93	63.33	78.98	N.R.	80.08

Note: N.R. implies not removed.

There may be several reasons for the difference in performance of reactor sites 23 and 24. One important reason is that while the reactors at site 24 have a definite residence time (7 days), but the reactors at site 23 have an indeterminate residence time. The reactors at site 23 were put together on an ad hoc basis, thus their residence times were not determined. Reactor 23 – 2, the plug flow reactor, did not have a regular flow through it. In the embedded reactor at site 23, 23 – 1 & 2, the flow was not controllable. Also, the feed stream at reactor site 23 had a significantly higher concentration of metals and lower pH (1 – 2) than that at reactor site 24 (pH 4 – 5). As discussed later, bioremediation may be a cumulative effect of sorption and bacterial remediation. The process of sorption is hindered by low pH. Low pH is also not suitable for bacterial growth, thus limiting bacterial remediation. Also, especially at reactor 23 – 1, if there was ever an interruption of flow due to any accidental reason, there would be an accumulation of highly contaminated water in the sampling tube, thus compromising the setup. All these factors together may have overwhelmed the biological material placed in these two reactors, rendering them ineffective. It is noted that due to inaccessibility of the site and overcommitted sampling personnel the reactor influent and effluent had to be sampled on the same day, whereas mean transit time through the reactors was seven days, i.e., the lag time was not taken into account. In that case, there might not be any direct connection between the effluent

and influent. This fact could account for concentrations of metals in the effluent that exceed the corresponding influent. The validity of the readings can be explained in the following manner: the readings were taken over a period of several weeks. As such, they represent average concentrations for both influents and effluents, and their general concentration trends. With regards to the carbon source, the Fairbanks area compost was seen to perform at par with the local peat except in the case of manganese. This can be explained as follows: manganese reacts to large chain hydrocarbons mainly by sorption (Webb et al, 1998). Local peat at Red Dog Mine was observed to be denser than Fairbanks area compost. Greater density could also translate to a greater reactive surface area for sorption reactions, which may be a reason why peat performed better. Also, remobilization of manganese may occur under anoxic or reducing conditions (Christensen et al., 1996). The biomass in the bioreactors is completely submerged in water, thus restricting access of oxygen to the biomass and creating reducing conditions. Such conditions may have mobilized manganese already native to the local peat, rendering removal ineffective. It can also be seen that in some cases, when the influent concentration to site 24 is high (Tables 4.1 through 4.5), the reactors perform well by removing metals. But if the concentrations drop, the effluent sample concentrations go up and sometimes exceed the influent concentrations. This is probably due to the fact that as a significant portion of the metal removal occurs by sorption reactions, a drop in the influent concentrations would cause the metals to de-sorb from the compost and dissolve into the water in the sample tube causing a much higher concentration. In addition to this factor, the time lag inherent to the reactor design may also have contributed to the discrepancy in concentrations of metals in influent and effluent.

In an experiment open to the influences of nature as those conducted at Red Dog reactor sites 23 and 24, many factors like temperature, precipitation etc. are not under control. The concentrations of all for the influent to reactor 24 on 08/14/2004, for example, were influenced by heavy rainfall just prior to that date. This lack of control may explain why some of the data do not conform to expectation.

Table 4.6 shows the data for the bench scale bioremediation replication. We see several orders of magnitude (1 to 3) removal of metals from the influent water, demonstrating the principle of bioremediation in bench scale experiments. Also significantly, in this and all other bench scale tests, the influent pH, which was usually in the range of 3 – 3.5 was raised to near neutral (6.5 – 6.8). `As pH is raised, some heavy metals might form insoluble oxides or hydroxides and precipitate out of solution. This process aids the bioremediation process.

Figures 4.1 through 4.5 represent the effect of the quantity of compost on metal removal. In the case of the metals lead, zinc and cadmium, a very specific and anticipated trend is seen, that of concentrations of metals slowly decreasing as the amount of compost is increased. In the case of iron, an exception is noted. The first sample in the first replicate (for 20 gm of compost) is seen to have a concentration higher than expected. The remaining samples in the first replicate, however, conform to the trend. In the second replicate for iron, the first two samples, for 20gm and 16 gm of compost weight, are seen to have high concentrations. But the subsequent samples are seen to conform to the same trend. The reason for this observation may be that the compost might not be homogenous in composition. The lack of homogeneity may have introduced excess iron in the experiments mentioned, resulting in higher-than-expected concentrations of iron in the effluents. In the case of manganese, there is no clear trend visible. This is because as stated above, manganese reacts primarily by sorption, which is a rapid reaction. Also, the compost has the requisite surface area, even in lesser quantities by weight, to accommodate manganese in the batch system. This is why change in time or quantity of compost has little effect on manganese removal, with the given influent conditions.

Figures 4.6 through 4.10 represent the experiments for residence time. Unfortunately no clear trend emerged from the data. But in most cases it is clear that remediation has occurred, as the influent concentration is greater than that of the effluent. This indicates the bioremediation in this set of experiments has been rapid.

The results for the sorption experiments in Table 4.7 show a general reduction in metal concentration from the influent to the effluent, excepting lead and manganese. The reduction in concentration in the cases of zinc, cadmium and iron are summarized in Table 4.9. The influent concentrations for the three metals are given in the first unshaded column. The effluent concentrations as mean and standard deviation are displayed in the next two columns respectively. The last column, displaying "Percent Removed" represents the percentage of the influent concentration that has been removed by the sorption process, based on the mean effluent concentration.

Table 4.10: Summary of Reduction of Metals in Sorption Experiment

Metals	Influent	Effluent		Percent
	(ppm)	Mean (ppm)	St. Dev. (ppm)	Removed
Zn	1027.88	587.77	184.35	42.82
Cd	1.03	0.59	0.18	42.82
Fe	39240.00	1613.38	507.71	95.89

It can be observed that iron, in this case, is almost entirely removed by sorption, while more than 40 % of zinc and cadmium are removed by the same process. We can therefore conclude that the primary process by which iron is removed, under the specific conditions of temperature, pressure, biomass and influent characteristics, is sorption. Sorption of zinc and cadmium may have been suppressed by competition with other ions, e.g., iron. It may also be that zinc and cadmium may have achieved their full potential for sorption under the laboratory conditions, and any further removal would invoke bacterial remediation. Lead and manganese do not show a general trend of reduction after sorption. The lack of such a trend may indicate that formation of sulphides, which is essential to conventional bioremediation, may not be happening in the cases of lead and manganese. This may have reduced the total efficiency of the sorption reactions.

Table 4.8 displays the results for the digestion experiment. It can be immediately observed that the concentration values for iron are high. This may have happened due to accidental contamination of the samples by an external source of iron. The negative values for some of the metals for the first two samples, viz., "Blank" and "2-AL" can be explained by the fact that in both the cases, the samples were expected to have low concentrations of the metals. A low concentration of metals caused the ICP-MS to operate below the calibration curve, thus generating negative values. For lead and zinc, it is seen that the unreacted compost, designated by "3-MB" and "4-MB", contains less metal than the compost after being utilized in remediation. This conforms to the expected pattern. Cadmium was not detected at any significant level during this experiment. Manganese, however, showed the opposite trend, containing more metal in the unreacted compost than the reacted compost samples. The reason for this trend may be that remobilization of manganese from the biomass into water may have occurred (Christensen et al., 1996). This is also supported by data for manganese in Table 4.6, where it is seen that the range for effluent concentration of manganese is 36.30 - 142.07 ppm with an influent concentration of 77.8 ppm, suggesting that manganese has been leached into the water from the biomass.

4.3 Results for Freeze Concentration

Freeze concentration results are displayed below. Table 4.11 gives the results for the experiments conducted with a cylindrical freezing vessel and artificially doped water. The cores of the samples were analyzed. The influent concentrations for these experiments are tabulated in Table 3.2.

Table - 4.11: Cylindrical Doped Water Freeze Concentration Results

Sample Designation	Temp. Frozen (C)	Metal	Concentration ppm
PbCore - 1	-10	Pb	30231.00
ZnCore - 1	-10	Zn	6394.65
FeCore - 1	-10	Fe	531.15
CdCore - 1	-10	Cd	8611.47
PbCore - 2	-20	Pb	27159.00
ZnCore - 2	-20	Zn	9148.54
FeCore - 2	-20	Fe	10723.03
CdCore - 2	-20	Cd	8290.00

Table 4.12 enumerates the data for the top down freezing experiments at -38 °C. In the shaded left column, the sample numbers with suffix "Top" indicate that the sample has been collected from the top of the frozen slab, from which the freezing front propagates downwards, rendering this a rarified concentration zone. Similarly the suffix "Bottom" indicates that the samples were collected from the end of the sample toward which the freeze front progresses. The initial concentration of the water used for the experiments at – 15 °C are the same as shown in Table 4.7 as the influent water for the sorption experiments. The concentrations for the influent water at – 38 °C is not available. Since the aim for this experiment was to determine the relative concentrations at the top and bottom of the frozen bulk solution, the initial concentrations of metals in the influent water was not deemed very important. The concentrations of the metals were expected to be lower toward the top of the slab and higher toward the bottom.

Table – 4.12: Top Down Freeze Concentration Results (-38 °C)

Sample Designation	Concentrations of metals in ppm				
	Pb	Zn	Cd	Fe	Mn
1A-Top	16.06	7818.00	11.53	23.33	46.50
1A-Bottom	22.97	19471.20	74.11	71.58	164.80
3A-Top	19.01	11396.40	23.11	74.19	100.90
3A-Bottom	24.60	26466.00	56.67	85.43	255.90
3B-Top	10.34	7506.60	18.33	32.80	43.50
3B-Bottom	25.42	18331.80	179.87	68.30	173.10

Results for a similar experiment carried out at -15 °C are tabulated below in Table 4.13.

Table – 4.13: Top Down Freeze Concentration Results (-15 °C)

Sample Designation	Concentrations of metals in ppm				
	Pb	Zn*	Cd	Fe*	Mn
6-A-Top	5.83	4810.30	3.63	449680.00	135.75
6-A-Bottom	53.38	40727.33	29.47	1916360.00	993.35
5-Top	11.03	11032.78	6.81	756570.00	218.56
5-Bottom	54.80	42516.67	29.00	2028320.00	1044.12

*Note:- These values may not be feasible, and may have occurred due to contamination from the drill bit.

Experiments performed at two different temperatures were compared as follows.
For every metal, the concentration of the sample designated "Top" was divided by that of the sample designated "Bottom", to obtain the ratio between the concentrations of the metal left in the top portion to that left on the bottom portion.
An example is given below:
In Table 4.11 –

$$\frac{\text{Concentration of Pb in1A - Bottom}}{\text{Concentration of Pb in 1A - Top}}$$

= 22.97 ppm / 16.06 ppm.

= 1.43.

This indicates that 1.43 times the amount of metal left in the top potion has traveled towards the bottom and is concentrated there.

Similarly,

$$\frac{Pb\,[3A - Bottom]}{Pb\,[3A - Top]} = 24.60 \text{ ppm} / 19.01 \text{ ppm} = 1.29.$$

and $$\frac{Pb\,[3B - Bottom]}{Pb\,[3B - Top]} = 25.42 \text{ ppm} / 10.34 \text{ ppm} = 2.46.$$

The numbers 1.43, 1.29 and 2.46 were then averaged over 3 (for the three pairs of samples available)

or, $$\frac{1.43 + 1.29 + 2.46}{3} = 1.73.$$

It can then be said that for the experiment conducted at -38 °C, 1.73 times the quantity of lead at the top of the frozen slab has traveled to the bottom of the slab. This process was repeated for all the samples for experiments conducted at two temperatures. The results are shown in Table 4.14.

Table 4.14: Comparative Performance of Freeze Front Experiments at -15 °C and - 38 °C

Temperature	Bottom Concentration as Mean Multiple of Top Concentration for				
Frozen (C)	Pb	Zn	Cd	Fe	Mn
-38	1.73	2.42	6.23	2.10	3.35
-15	7.08	6.18	6.18	3.47	6.05

4.3.1 Discussion of the Results for Freeze Concentration

The data for these experiments show a trend toward higher concentration in the volumes which should theoretically show higher concentration. In the case of Table 4.11, the concentrations of the metals are high. Considering the fact that a diameter of only 5/8″ was cored out from the samples, the concentrations displayed are too high to have originated solely from the contaminated water. It is surmised that the drill bit,

which had been previously used to drill metal, may have contributed extraneous metal to the samples.

In Table 4.12 and Table 4.13, there is a clear trend of the concentration at the top being lower than that at the bottom. The samples were initially frozen rapidly (-38 °C). It can therefore be concluded that the freezing front, while propagating downward, drives a part of the total metal content ahead of it. But due to fast freezing, the solutes may not have had adequate time to move out of solution. This can be supported by the data from the experiment conducted at – 15 °C. Table 4.13 gives a measure of the relative efficiency of freezing at – 38 °C and – 15 °C. It is evident from Table 4.14 that, on an average, a greater multiple of the amount of metal at the rarified top end is present at the concentrated bottom end. This may be due to the fact that the slower freezing front at – 15 °C gives more time for the solutes to leave the solution and concentrate at the bottom end.

4.4 Results for Reverse Osmosis

The results for the reverse osmosis experiments are tabulated below in Table 4.9. In the table, sample designation "DK-feed 9:1" represents the concentrations of the target metals in the feed solution (after a 9 : 1 dilution with deionized water). "DK-raw" represents the concentrations of the metals in the original undiluted feedstock. These are baseline determinations for reference. The same feed solution at 9:1 dilution was used for DK and ADF membranes. Other sample designations like "DK-1-9/1" or "ADF-2-9/1" represent the type of the membrane used, the sample number on that membrane and the dilution, in this case 9:1. The pressures at which permeates were obtained is given for each run, and the throughput is calculated based on volumetric measurement of the effluent with time through the effective surface area of filtration, in this case calculated to be 80.12 sq. cm.

Table 4.15: Reverse Osmosis Experiment Data

Sample Designation	Pressure (psi)	Flow liter/hr	PERMEATE CONCENTRATIONS (ppm)				
			Pb	Zn	Cd	Fe	Mn
DK-Raw	N/A	N/A	20.62	8779.20	24.82	21.88	60.29
DK-feed 9:1	N/A	N/A	1.41	307.55	1.94	16.13	11.53
DK-1-9/1	260	28.70	0.03	0.32	0.00	33.75	0.04
DK-2-9/1	300	78.03	0.02	0.12	0.00	17.98	0.02
DK-3-9/1	350	83.67	0.02	0.12	0.00	20.21	0.01
DK-4-9/1	400	114.33	0.02	0.14	0.00	17.06	0.01
DK-5-9/1	450	133.10	0.02	0.15	0.00	15.97	0.01
DK-6-9/1	500	154.94	0.02	0.11	0.00	13.44	0.01
ADF-1-9/1	700	28.38	0.00	0.03	0.00	0.10	0.00
ADF-2-9/1	750	41.88	0.00	0.01	0.00	0.08	0.00
ADF-3-9/1	800	54.16	0.00	0.01	0.00	0.07	0.00

Data for the experiment with a spiral membrane is given in Table 4.16. In this experiment an AD class membrane was used. Diluted mine water (with 9 parts deionized water and 1 part mine water) and raw or undiluted water were used as feed in this experiment.

Table 4.16: Reverse Osmosis Experiment with Spiral AD Membrane

Sample Designation	Pressure (psi)	Flow liter/hr/sq. m	PERMEATE CONCENTRATIONS (ppm)				
			Pb	Zn	Cd	Fe	Mn
For Diluted Feed (9 parts D.I. Water to 1 part mine water)							
Feed	N/A	N/A	1.42	54.26	0.04	749.50	2.05
Permeate AD-1	200	5.75	0.00	0.12	0.01	5.67	0.00
Permeate AD-2	300	7.84	0.00	0.10	0.01	5.66	0.00
Permeate AD-3	400	15.29	0.00	0.08	0.01	1.69	0.00
Permeate AD-4	485	16.73	0.00	0.21	0.02	6.49	0.01
For Raw Feed (Undiluted mine water)							
Feed	N/A	N/A	7.29	4574.73	1.81	13376.60	17.42
Permeate AD-5	120	3.32	0.00	0.63	0.00	71.72	0.02
Permeate AD-6	190	5.87	0.01	0.82	0.00	29.25	0.03
Permeate AD-7	300	10.27	0.01	0.68	0.00	27.57	0.02
Permeate AD-8	395	14.88	0.01	0.63	0.00	22.66	0.02
Permeate AD-9	475	16.70	0.01	1.15	0.00	36.35	0.02

4.4.1 Discussion of the Results for Reverse Osmosis

It is indicated in the data that there is a large percentage removal from the influent water. There are several degrees of magnitude reduction in the concentration of the metals. From the membrane specifications it is seen that ADF is the tighter of the two membranes. This is also demonstrated by the higher working pressure of the ADF membrane. But ADF compensates by removing almost 100 % of the metals in every case. As anticipated, the data also shows an increase in throughput with the increase in working pressure. But it also indicates that at high working pressures, the membrane integrity holds. If high pressure had damaged the membrane there would have been a sudden spike in the concentrations of the metals, which does not occur. There is some anomalous data recorded in the case of iron. This is thought to be due to contamination of the effluent by external iron, which leaches into the water from the steel pressure vessels in which the membrane is placed during filtration. Deionized water, which is used as a dilutant, is slightly acidic and will cause iron to be dissolved in it. Yet another factor indication contamination from the steel block is that if there had been a general contamination problem due to mishandling, all the other metals, especially lead and zinc, would also have shown elevated levels.

Table 4.15 shows that the tight AD membrane removed almost 100% of the metals from the feed. Results for iron are found to be higher than expected, which may be due to the reason stated above. It is to be noted that there is very little change in the removal efficiency of the membrane for both the diluted and the undiluted feed. This establishes that reverse osmosis can be efficiently used for metal removal from highly contaminated water.

CHAPTER V
CONCLUSIONS AND FUTURE WORK

In this chapter, conclusions drawn from the experiments conducted and data collected will be presented. Analysis of the data, already conducted in Chapter IV, will be presented as a coherent synopsis and the lessons learned will be discussed. Future possibilities of research will be presented.

5.1 Conclusions: Bioremediation

The biggest advantage for bioremediation as a technique to decontaminate water is that it can be implemented cost effectively by the mining industry. At the beginning of a surface mining operation, trees and shrubs need to be cleared. The plant materials from clearing and grubbing can be easily used to jump-start bioremediation. As has been exemplified in the lab scale studies and the pilot scale study for reactor site 24, metals can be reduced to a significant extent using the basic reaction principles of bioremediation. The problem that the lab scale studies give rise to is predictability. As in the case of conventional chemical treatment, one can precisely predict the resultant concentration of a metal when it passes thorough each step in the chain of chemical unit processes. This advantage is not afforded to the designers in the planning stage of bioremediation, as, unlike the chemicals added in conventional treatment, biomass in bioremediation does not have uniform chemical composition. A reasonable estimate of performance can be arrived at after conducting a series of tests on the biomass and on the influent water available, but this requires extra steps in planning and permitting. Also, as shown by the data, a good result in lab scale tests does not necessarily guarantee a similar result in the field. Lack of control on field conditions like temperature, pH, influent concentrations and flow rate can also cause difficulties in predicting the performance of bioreactors in the field. Variations in the aforementioned conditions may have been the cause of the anomalous data in the pilot scale experiments at Red Dog. The anomalies in the data in the field experiment raise questions about the consistency of performance of the method; consequently the "scaling up" factor from the lab scale to the field scale and thence to the industrial

scale becomes an important point. Need is also felt to standardize the biomass characteristics with certain parameters so that there can be ready sources of such material available to any mine which wants to implement the process. Failing that, test parameters must be set for plant material that are locally available and usable, so that the mine management can, with a series of test, arrive at a conclusion as to the efficiency of the biomass in bioremediation. This will cut cost and make the process more amenable to diverse needs.

5.2 Conclusions: Freeze Concentration

Freeze concentration is a process that has limited application based on the geography of the area in which the mine is situated. Cold places like Alaska could very well implement such a method as the ambient temperature would be favorable. The principle of freeze concentration is simple and examples of it are readily available in nature and daily life. As the data shows there is some concentration of the solutes or contaminants ahead of the freezing front and some purification is achieved. The degree of purification achieved may present the industry with an incentive to try to implement the system. The technical difficulty in this method is to keep the desired freezing front dominant in the bulk solution, while minimizing the effect of other freezing fronts. Another important problem is that of separating the cleaner ice from the frozen bulk.

5.3 Conclusions: Reverse Osmosis

Reverse osmosis is a method of purification nowadays used only in situations requiring a high purity product. It is deemed an expensive technique because of the high capital and operating costs. The membranes used in reverse osmosis are fragile and expensive to maintain. The setup is temperature sensitive; in a place like Alaska it would have to be housed in a specially heated enclosure. Reverse osmosis is very sensitive to fouling of the membranes by bacterial growth or influx of large particles. Once the membrane is so damaged, it can be cleaned to restore performance, but it has to be eventually replaced. It is also an indiscriminate method, removing everything larger that its rejection size. For example, a desalination membrane will

remove sodium ions along with everything else, though sodium may not be an important contaminant. But the data shows that given the right kind of chemical ambiance, reverse osmosis can remove almost all of the offending ions, and produce discharge-ready water. With the EPA regulations pushing metal discharge limits progressively lower, high end filtration methods like reverse osmosis may be a major source of treatment for the mining industries of the future.

5.4 Future Work

Future work in bioremediation could focus primarily on standardizing the components of the technology. In order to achieve standardization, the most important focus would be to standardize the characteristics of the biomass used. A set of simple tests developed to examine the properties of the biomass would give an interested party a reasonable idea as to the efficiency of the biomass in removing metals, both bacterially and through sorption. Specific work should also be done on the bacteria involved in remediation, and steps should be taken to introduce such cultures into field environments and monitor them. As bacterial cultures are not difficult to make and transport, introducing them would cut down on the time taken for bacterial remediation to begin. Lastly, through numerous experiments, the lab data should be effectively scaled up to the field and thence to the industrial scale.

Future work in freeze concentration would largely entail the investigation of the effect of different freezing rates and container (pond) shapes and sizes have on the concentration of the contaminants in a particular location. The effect of macroscopic suspended particles on freezing should also be taken into account.

An important variable in reverse osmosis is the characteristics of the membrane used. Making cheaper but effective membranes would be an important step toward making the technology financially accessible to all. Keeping in mind the propensity of the membrane to foul with macro particles, a composite membrane module, with membranes in series in the order of permeability, capable of handling a large range of particle sizes would make the technology attractive to the industrial buyer.

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